APPENDIX B

IMPORTANT PROCESSES AFFECTING THE FATE AND TRANSPORT OF ORGANIC COMPOUNDS IN THE SUBSURFACE

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INTRODUCTION

B.1.1 FATE AND TRANSPORT MECHANISMS

This appendix presents an overview of the important processes affecting the fate and transport of chlorinated solvents and fuel hydrocarbons dissolved in ground water. The environmental fate and transport of a contaminant is controlled by the compound's physical and chemical properties and the nature of the subsurface media through which the compound is migrating. Several processes are known to cause a reduction in the concentration and/or mass of a contaminant dissolved in ground water. Those processes that result only in the reduction of a contaminant's concentration but not of the total contaminant mass in the system are termed "nondestructive." Those processes that result in degradation of contaminants are referred to as "destructive." Nondestructive processes include advection, hydrodynamic dispersion (mechanical dispersion and diffusion), sorption, dilution, and volatilization. Destructive processes include biodegradation and abiotic degradation mechanisms. Biodegradation may be the dominant destructive attenuation mechanism acting on a contaminant, depending upon the type of contaminant and the availability of electron donors or carbon sources. Abiotic degradation processes are also known to degrade chlorinated solvents; where biodegradation is not occurring, these may be the only destructive processes operating. However, the rates of abiotic processes are generally slow relative to biodegradation rates.

Remediation by monitored natural attenuation results from the integration of all the subsurface attenuation mechanisms (both nondestructive and destructive) operating at a given site. Table B.1.1 summarizes the processes that affect fate and transport of chlorinated solvents and fuel hydrocarbons dissolved in ground water. Important factors to consider include:

- The compound's soil/water distribution coefficient (K_d);
- The compound's organic carbon/water partition coefficient (K_{oc});
- The compound's octanol/water partition coefficient (K_{ow});
- The compound's water solubility;
- The compound's vapor pressure;
- The compound's Henry's Law constant (air/water partition coefficient, H);
- Indigenous bacterial population;
- Hydraulic conductivity of aquifer materials;
- Porosity of aquifer materials;
- Total organic carbon content of aquifer materials;
- Bulk density of aquifer materials;
- Aquifer heterogeneity; and
- Ambient ground-water geochemistry.

Nondestructive attenuation mechanisms are discussed in Section B-2. Biodegradation is discussed in Section B-3. Abiotic degradation mechanisms are discussed in Section B-4. It is important to separate nondestructive from destructive attenuation mechanisms during the natural attenuation demonstration. The methods for correcting apparent attenuation caused by nondestructive attenuation mechanisms are discussed in Appendix C.

B.1.2 MATHEMATICAL DESCRIPTION OF SOLUTE FATE AND TRANSPORT

The partial differential equation describing contaminant migration and attenuation in the saturated zone includes terms for advection, dispersion, sorption, and degradation. In one dimension, the partial differential equation describing solute transport in the saturated zone is:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} \pm Q_s \qquad \text{eq. B.1.1}$$

Table B.1.1 *Summary of Important Processes Affecting Solute Fate and Transport*

Process	Description	Dependencies	Effect
Advection	Movement of solute by bulk ground-water movement.	Dependent on aquifer properties, mainly hydraulic conductivity and effective porosity, and hydraulic gradient. Independent of contaminant properties.	Main mechanism driving contaminant movement in the subsurface.
Dispersion	Fluid mixing due to ground-water movement and aquifer heterogeneities.	Dependent on aquifer properties and scale of observation. Independent of contaminant properties.	Causes longitudinal, transverse, and vertical spreading of the plume. Reduces solute concentration.
Diffusion	Spreading and dilution of contaminant due to molecular diffusion.	Dependent on contaminant properties and concentration gradients. Described by Fick's Laws.	Diffusion of contaminant from areas of relatively high concentration to areas of relatively low concentration. Generally unimportant relative to dispersion at most ground-water flow velocities.
Sorption	Reaction between aquifer matrix and solute whereby relatively hydrophobic organic compounds become sorbed to organic carbon or clay minerals.	Dependent on aquifer matrix properties (organic carbon and clay mineral content, bulk density, specific surface area, and porosity) and contaminant properties (solubility, hydrophobicity, octanol-water partitioning coefficient).	Tends to reduce apparent solute transport velocity and remove solutes from the ground water via sorption to the aquifer matrix.
Recharge (Simple Dilution)	Movement of water across the water table into the saturated zone.	Dependent on aquifer matrix properties, depth to ground water, surface water interactions, and climate.	Causes dilution of the contaminant plume and may replenish electron acceptor concentrations, especially dissolved oxygen.
Volatilization	Volatilization of contaminants dissolved in ground water into the vapor phase (soil gas).	Dependent on the chemical's vapor pressure and Henry's Law constant.	Removes contaminants from ground water and transfers them to soil gas.
Biodegradation	Microbially mediated oxidation-reduction reactions that degrade contaminants.	Dependent on ground-water geochemistry, microbial population and contaminant properties. Biodegradation can occur under aerobic and/or anaerobic conditions.	May ultimately result in complete degradation of contaminants. Typically the most important process acting to truly reduce contaminant mass.
Abiotic Degradation	Chemical transformations that degrade contaminants without microbial facilitation; only halogenated compounds are subject to these mechanisms in the ground-water environment.	Dependent on contaminant properties and ground-water geochemistry.	Can result in partial or complete degradation of contaminants. Rates typically much slower than for biodegradation.
Partitioning from NAPL	Partitioning from NAPL into ground water. NAPL plumes, whether mobile or residual, tend to act as a continuing source of ground-water contamination.	Dependent on aquifer matrix and contaminant properties. as well as ground-water mass flux through or past NAPL plume.	Dissolution of contaminants from NAPL represents the primary source of dissolved contamination in ground water.

Where:

C = solute concentration [M]

t = time [T]

D_x = hydrodynamic dispersion [L^2/T]

R = coefficient of retardation [dimensionless]

x = distance along flow path [L]

v_x = transport velocity in x direction [L/T]

Q_s = general source or sink term for reactions involving the production or loss of solute (e.g., biodegradation) [$M/L^3/T$]

The degradation of organic contaminants commonly can be approximated using first-order kinetics. In one dimension, the partial differential equation describing solute transport with first-order decay in the saturated zone is given by:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. B.1.2}$$

Where:

C = concentration [M/L^3]

t = time [T]

D_x = hydrodynamic dispersion [L^2/T]

x = distance along flow path [L]

R = coefficient of retardation [dimensionless]

v_x = transport velocity in x direction [L/T]

λ = first-order decay rate [T^{-1}]

These equations serve to illustrate how the processes of advection, dispersion, sorption, and biotic and abiotic degradation are integrated to describe the fate and transport of solutes in the saturated zone. These relationships were derived using the continuity (conservation of mass) equation, which states that the rate of change of contaminant mass within a unit volume of porous media is equal to the flux of contaminant into the unit volume minus the flux out of the unit volume (Freeze and Cherry, 1979). Processes governing flux into the unit volume include advection and hydrodynamic dispersion (including mechanical dispersion and diffusion). Processes governing flux out of the unit volume include advection, hydrodynamic dispersion, dilution, sorption, and chemical reactions (most notably biodegradation). The change in solute concentration may, therefore, be stated mathematically as:

Change in Solute Concentration = Flux In - Flux Out ± Reactions

The following sections describe the most significant reactions affecting this mass balance (and therefore the fate and transport) of organic contaminants in the subsurface. Methods for evaluating the flux through the system will be discussed in Appendix C.

SECTION B-2
NONDESTRUCTIVE ATTENUATION MECHANISMS

B.2.1 ADVECTION

Advective transport is the transport of solutes by the bulk movement of ground water. Advection is the most important process driving dissolved contaminant migration in the subsurface. The linear groundwater velocity in the direction parallel to ground-water flow caused by advection is given by:

$$v_x = -\frac{K}{n_e}\frac{dH}{dL} \qquad \text{eq. B.2.1}$$

Where:

v_x = average linear velocity [L/T]
K = hydraulic conductivity [L/T]
n_e = effective porosity [L^3/L^3]
dH/dL = hydraulic gradient [L/L]

Solute transport by advection alone yields a sharp solute concentration front. Immediately ahead of the front, the solute concentration is equal to the background concentration (generally zero). At and behind the advancing solute front, the concentration is equal to the initial contaminant concentration at the point of release. This is referred to as plug flow and is illustrated in Figures B.2.1, B.2.2, and B.2.3. In reality, the advancing front spreads out due to the processes of dispersion and diffusion, as discussed in Section B-3, and is retarded by sorption and biodegradation, as discussed in Sections B-4 and B-5, respectively.

The one-dimensional advective transport component of the advection-dispersion equation is given by:

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} \qquad \text{eq. B.2.2}$$

Where:

v_x = average linear velocity [L/T]
C = contaminant concentration [M/L^3]
t = time [T]
x = distance along flow path [L]

Equation B.2.2 considers only advective transport of the solute. In some cases this may be a fair approximation for simulating solute migration because advective transport is the main force behind contaminant migration. However, because of dispersion, diffusion, sorption, and biodegradation, this equation generally must be combined with the other components of the modified advection-dispersion equation (equation B.1.1) to obtain an accurate mathematical description of solute transport.

B.2.2 HYDRODYNAMIC DISPERSION

Hydrodynamic dispersion is the process whereby a contaminant plume spreads out in directions that are longitudinal and transverse to the direction of plume migration. Dispersion of organic solutes in an aquifer is an important consideration when modeling remediation by natural attenuation. Dispersion of a contaminant dilutes the concentrations of the contaminant, and introduces the contaminant into relatively pristine portions of the aquifer where it may admix with more electron acceptors crossgradient to the direction of ground-water flow. Two very different processes cause

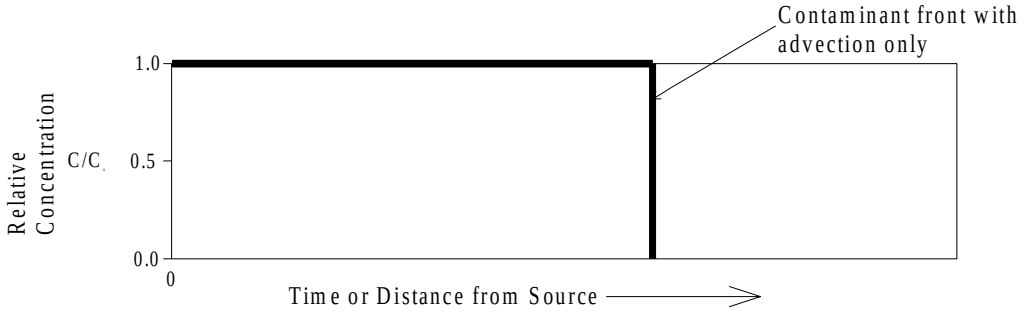

Figure B.2.1 *Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only.*

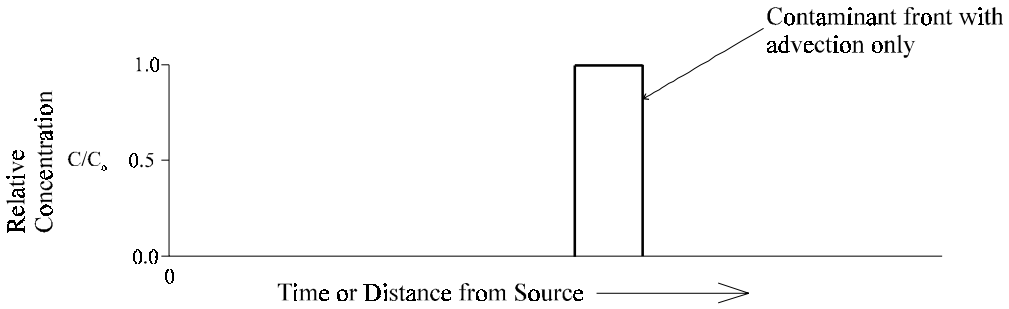

Figure B.2.2 *Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only.*

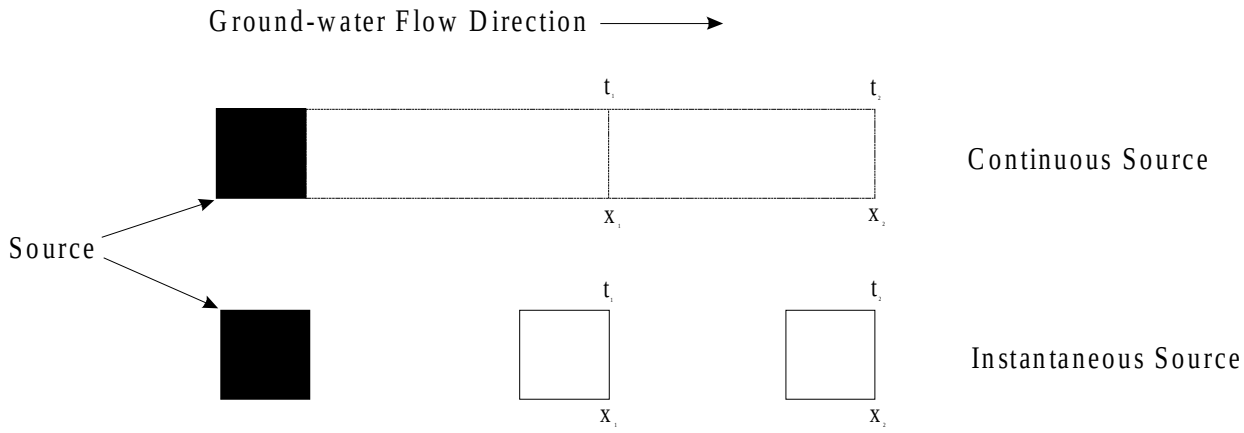

Figure B.2.3 *Plume migration in two dimensions (plan view) showing plume migration resulting from advective flow only with continuous and instantaneous sources.*

hydrodynamic dispersion; mechanical dispersion and molecular diffusion. The variable describing hydrodynamic dispersion, D, is the sum of mechanical dispersion and molecular diffusion. Mechanical dispersion is the dominant mechanism causing hydrodynamic dispersion at normal ground-water velocities. At extremely low ground-water velocities, molecular diffusion can become the dominant mechanism of hydrodynamic dispersion. Molecular diffusion is generally ignored for most ground-water studies. The following sections describe these processes and how they are incorporated into the modified advection-dispersion equation (Equation B.1.1).

B.2.2.1 Mechanical Dispersion

As defined by Domenico and Schwartz (1990), mechanical dispersion is mixing that occurs as a result of local variations in velocity around some mean velocity of flow. With time, a given volume of solute will gradually become more dispersed as different portions of the mass are transported at the differing velocities. In general, the main cause of variations of both rate and direction of transport velocities is the heterogeneity of the porous aquifer medium. These heterogeneities are present at scales ranging from microscopic (e.g., pore to pore) to macroscopic (e.g., well to well) to megascopic (e.g., a regional aquifer system).

Three processes are responsible for mechanical dispersion on the microscopic scale (Figure B.2.4). The first process is the variation in flow velocity through pores of various sizes. As ground water flows through a porous medium, it flows more slowly through large pores than through smaller pores. The second cause of mechanical dispersion is tortuosity, or flow path length. As ground water flows through a porous medium, some of the ground water follows less tortuous (shorter) paths, while some of the ground water takes more tortuous (longer) paths. The longer the flow path, the slower the average linear velocity of the ground water and the dissolved contaminant. The final process causing mechanical dispersion is variable friction within an individual pore. Groundwater traveling close to the center of a pore experiences less friction than ground water traveling next to a mineral grain, and therefore moves faster. These processes cause some of the contaminated ground water to move faster than the average linear velocity of the ground water and some to move slower. This variation in average velocity of the solute causes dispersion of the contaminant.

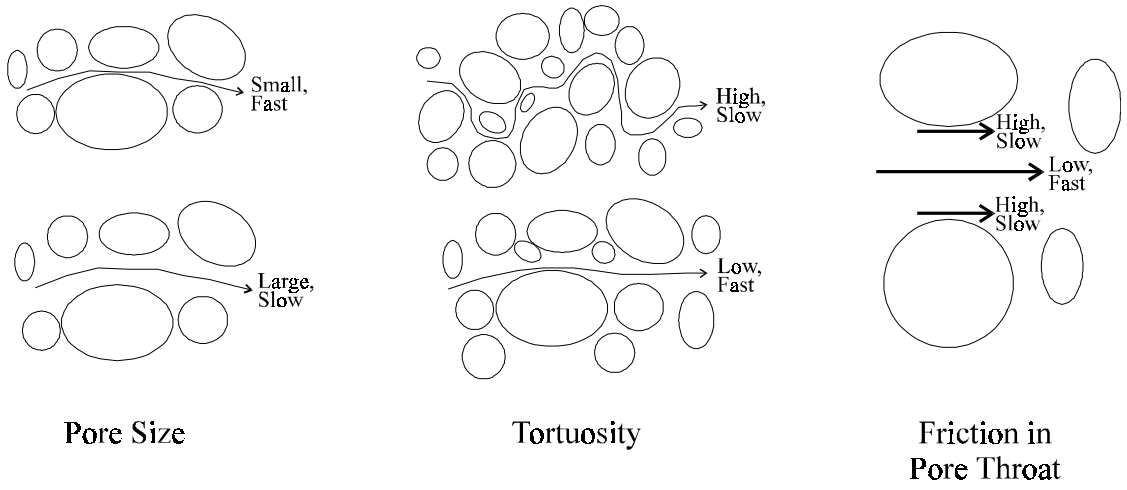

Figure B.2.4 *Physical processes causing mechanical dispersion at the microscopic scale.*

Heterogeneity at the macroscopic and megascopic scales also creates variability in ground water and solute velocities, therefore producing dispersion on a larger scale. Geologic features that con-

tribute to dispersion at the macroscopic scale include stratification characteristics such as changing unit geometry, discontinuous units, and contrasting lithologies, and permeability characteristics such as nonuniform permeability, directional permeability, and trending permeability (Domenico and Schwartz, 1990). Even in aquifer material that appears to be homogeneous, relatively small changes in the fraction of fine sediment can change hydraulic conductivity characteristics enough to produce significant variations in fluid and solute velocities and thus introduce dispersion. Larger geological features will introduce dispersion at the megascopic scale. At this scale, structural features such as faults, dipping strata, folds, or contacts will create inhomogeneity, as will stratigraphic features such as bedding or other depositional structures.

As a result of dispersion, the solute front travels at a rate that is faster than would be predicted based solely on the average linear velocity of the ground water. The overall result of dispersion is spreading and mixing of the contaminant plume with uncontaminated ground water. Figures B.2.5 and B.2.6 illustrate the effects of hydrodynamic dispersion on an advancing solute front. The component of hydrodynamic dispersion contributed by mechanical dispersion is given by the relationship:

$$Mechanical\ Dispersion = \alpha_x v_x \qquad \text{eq. B.2.3}$$

Where:

v_x = average linear groundwater velocity [L/T]

α_x = dispersivity [L]

Mechanical dispersion has two components, longitudinal dispersion and transverse (both horizontal and vertical) dispersion. Longitudinal dispersion is the spreading of a solute in a direction parallel to the direction of ground-water flow. On the microscopic scale, longitudinal dispersion

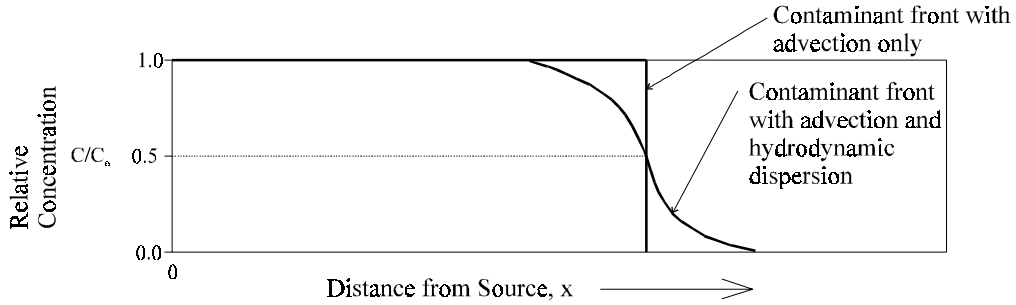

Figure B.2.5 *Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only and the combined processes of advection and hydrodynamic dispersion.*

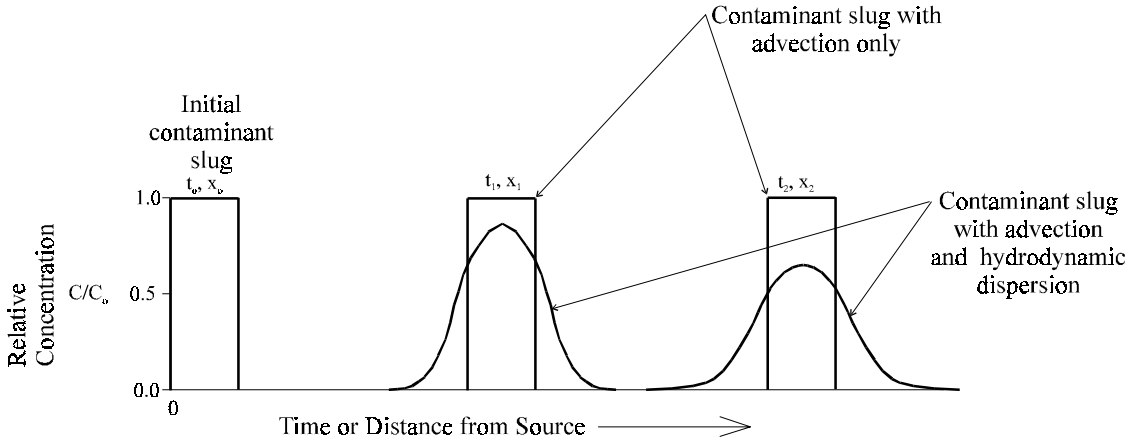

Figure B.2.6 *Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only and the combined processes of advection and hydrodynamic dispersion.*

occurs because of velocity changes due to variations in pore size, friction in the pore throat, and tortuosity. Transverse dispersion is the spreading of a solute in directions perpendicular to the direction of ground-water flow. Transverse dispersion on the microscopic scale is caused by the tortuosity of the porous medium, which causes flow paths to branch out from the centerline of the contaminant plume.

B.2.2.2 Molecular Diffusion

Molecular diffusion occurs when concentration gradients cause solutes to migrate from zones of higher concentration to zones of lower concentration, even in the absence of ground-water flow. Molecular diffusion is only important at low ground-water velocities, and therefore can be ignored in areas with high ground-water velocities (Davis *et al.*, 1993).

The molecular diffusion of a solute in ground water is described by Fick's Laws. Fick's First Law applies to the diffusive flux of a dissolved contaminant under steady-state conditions and, for the one-dimensional case, is given by:

$$F = -D\frac{dC}{dx} \qquad \text{eq. B.2.4}$$

Where:

F = mass flux of solute per unit area of time [M/T]
D = diffusion coefficient (L^2/T)
C = solute concentration (M/L^3)
$\frac{dC}{dx}$ = concentration gradient ($M/L^3/L$)

For systems where the dissolved contaminant concentrations are changing with time, Fick's Second Law must be applied. The one-dimensional expression of Fick's Second Law is:

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2} \qquad \text{eq. B.2.5}$$

Where:

$\frac{dC}{dt}$ = change in concentration with time [M/T]

The process of diffusion is slower in porous media than in open water because the ions must follow more tortuous flow paths (Fetter, 1988). To account for this, an effective diffusion coefficient, D*, is used.

The effective diffusion coefficient is expressed quantitatively as (Fetter, 1988):

$$D^* = wD \qquad \text{eq. B.2.6}$$

Where:

w = empirical coefficient determined by laboratory experiments [dimensionless]

The value of *w* generally ranges from 0.01 to 0.5 (Fetter, 1988).

B.2.2.3 Equation of Hydrodynamic Dispersion

Hydrodynamic dispersion, D, has two components, mechanical dispersion and molecular diffusion. For one-dimensional flow, hydrodynamic dispersion is represented by the following equation (Freeze and Cherry, 1979):

$$D_x = \alpha_x v_x + D^* \qquad \text{eq. B.2.7}$$

Where:

D_x = longitudinal coefficient of hydrodynamic dispersion in the x direction [L^2/T]
α_x = longitudinal dispersivity [L]
v_x = average linear ground-water velocity [L/T]
D* = effective molecular diffusion [L^2/T]

Dispersivity is a parameter that is characteristic of the porous medium through which the contaminant migrates. Dispersivity represents the spreading of a contaminant over a given length of flow, and therefore has units of length. It is now commonly accepted (on the basis of empirical evidence) that as the scale of the plume or the system being studied increases, the dispersivity will also increase. Therefore, dispersivity is scale-dependent, but at a given scale, data compiled by Gelhar *et al*. (1985 and 1992) show that dispersivity may vary over three orders of magnitude. The data of Gelhar *et al*. (1992) are presented on Figure B.2.7 (with permission from Newell et al., 1996).

Several approaches can be used to estimate longitudinal dispersivity, α_x., on the field scale (i.e., macroscopic to megascopic scales). One technique involves conducting a tracer test. Although this is potentially the most reliable method, time and monetary constraints can be prohibitive. Another method commonly used to estimate dispersivity when implementing a solute transport model is to start with a longitudinal dispersivity of 0.1 times the plume length (Lallemand-Barres and Peaudecerf, 1978; Pickens and Grisak, 1981; Spitz and Moreno, 1996). This assumes that dispersivity varies linearly with scale. However, Xu and Eckstein (1995) evaluated the same data presented by Gelhar *et al*. (1992) and, by using a weighted least-squares method, developed the following relationship for estimating dispersivity:

$$\alpha_x = 0.83(Log_{10} L_P)^{2.414} \qquad \text{eq. B.2.8}$$

Where:

α_x = longitudinal dispersivity [L]

L_p = plume length [L]

Both relationships are shown on Figure B.2.7. In either case, the value derived for dispersivity will be an estimate at best, given the great variability in dispersivity for a given plume length. However, for modeling studies, an initial estimate is needed, and these relationships provide good starting points for a modeling study.

In addition to estimating longitudinal dispersivity, it may be necessary to estimate the transverse and vertical dispersivities (α_T. and α_Z., respectively) for a given site. Several empirical relationships between longitudinal dispersivity and transverse and vertical dispersivity have been described. Commonly, α_T is estimated as $0.1\alpha_x$. (based on data from Gelhar *et al*., 1992), or as $0.33\alpha_x$. (ASTM, 1995; US EPA, 1986). Vertical dispersivity (α_Z) may be estimated as $0.05\alpha_x$. (ASTM, 1995), or as $0.025\alpha_x$. to $0.1\alpha_x$. (US EPA, 1986).

Some solute transport modelers will start with an accepted literature value for the types of materials found in the aquifer matrix. After selecting initial dispersivity values, the contaminant transport model is calibrated by adjusting the dispersivities (along with other transport parameters, as necessary) within the range of accepted literature values until the modeled and observed contaminant distribution patterns match (Anderson, 1979). This is a two-step process. The first step is to calibrate the flow model to the hydraulic conditions present at the site. After the ground-water flow model is calibrated to the hydraulics of the system, the contaminant transport model is calibrated by trial and error using various values for dispersivity. There is no unique solution because several hydraulic parameters, including hydraulic conductivity, effective porosity, and dispersivity, are variable within the flow system (Anderson, 1979; Davis *et al*., 1993), and other transport parameters such as retardation and biodegradation may not be well-defined.

B.2.2.4 One-Dimensional Advection-Dispersion Equation

The advection-dispersion equation is obtained by adding hydrodynamic dispersion to equation B.2.2. In one dimension, the advection-dispersion equation is given by:

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \qquad \text{eq. B.2.9}$$

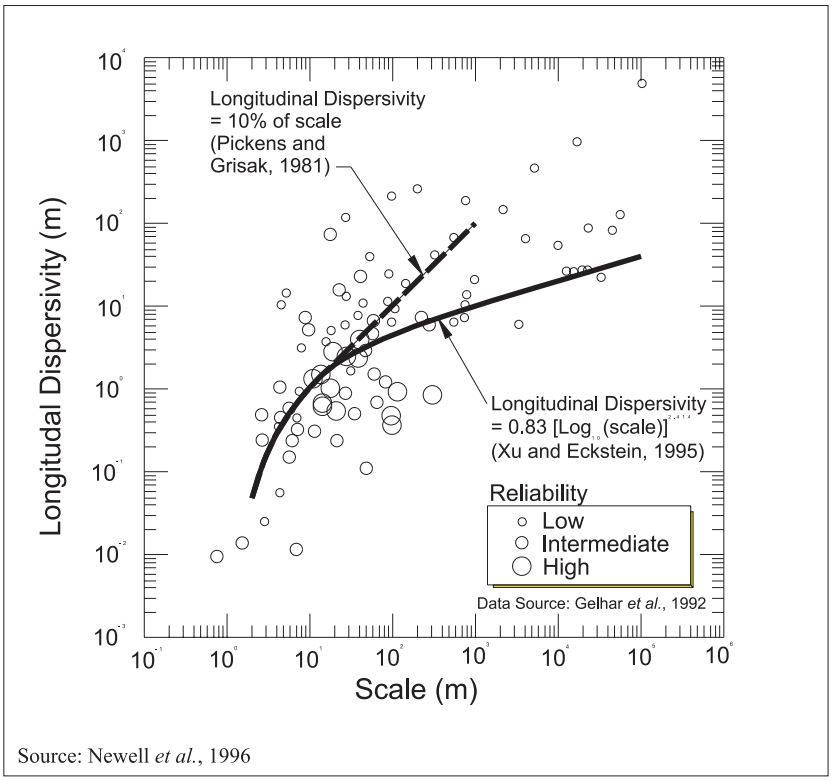

Figure B.2.7 *Relationship between dispersivity and scale.*

Where:

v_x = average linear velocity [L/T]
C = contaminant concentration [M/L^3]
D_x = hydrodynamic dispersion [L^2/T]
t = time [T]
x = distance along flow path [L]

This equation considers both advection and hydrodynamic dispersion. Because of sorption and biodegradation, this equation generally must be combined with the other components of the modified advection-dispersion equation presented as equation B.1.1 to obtain an accurate mathematical description of solute transport.

B.2.3 SORPTION

Many organic contaminants, including chlorinated solvents and BTEX, are removed from solution by sorption onto the aquifer matrix. Sorption is the process whereby dissolved contaminants partition from the ground water and adhere to the particles comprising the aquifer matrix. Sorption of dissolved contamination onto the aquifer matrix results in slowing (retardation) of the contaminant relative to the average advective ground-water flow velocity and a reduction in dissolved BTEX concentrations in ground water. Sorption can also influence the relative importance of volatilization and biodegradation (Lyman *et al.*, 1992). Figures B.2.8 and B.2.9 illustrate the effects of sorption on an advancing solute front.

Keep in mind that sorption is a reversible reaction and that at a given solute concentration, some portion of the solute is partitioning to the aquifer matrix and some portion is also desorbing and reentering solution. As solute concentrations change, the relative amounts of contaminant that are sorbing and desorbing will change. For example, as solute concentrations decrease (perhaps due to

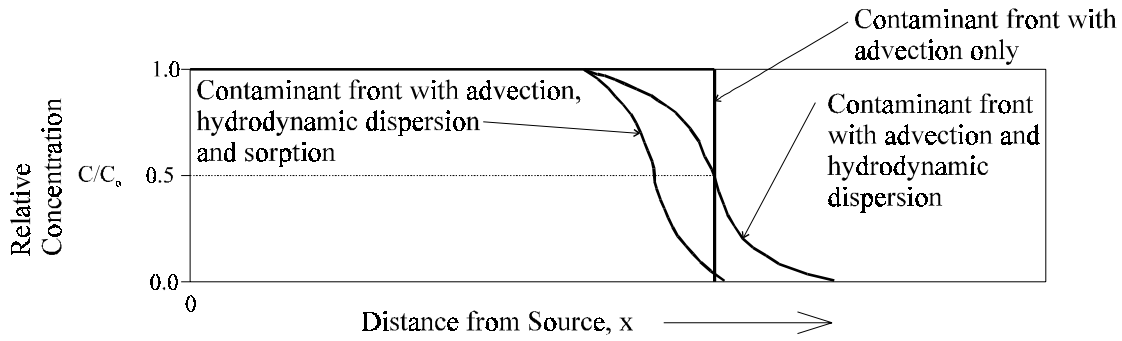

Figure B.2.8 *Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; and the combined processes of advection, hydrodynamic dispersion, and sorption.*

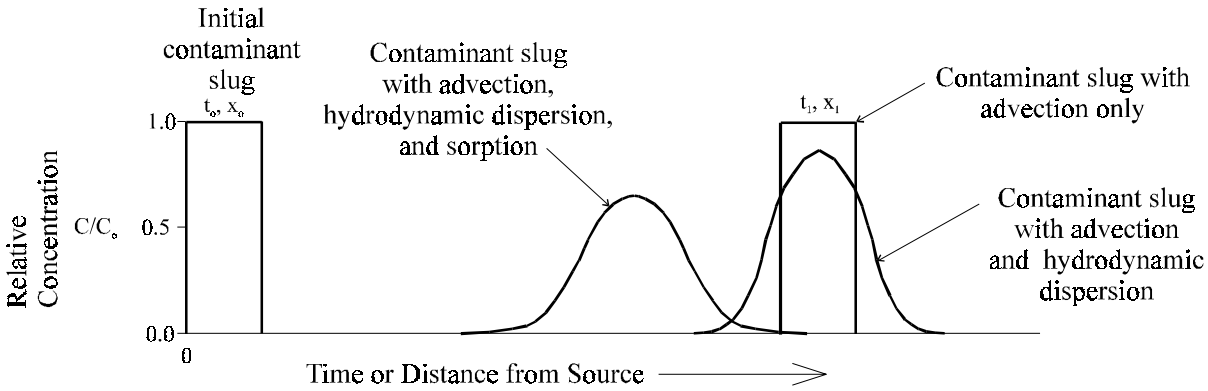

Figure B.2.9 *Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; and the combined processes of advection, hydrodynamic dispersion, and sorption.*

plume migration or solute biodegradation and dilution), the amount of contaminant reentering solution will likely increase. The affinity of a given compound for the aquifer matrix will not be sufficient to permanently isolate it from ground water, although for some compounds, the rates of desorption may be so slow that the loss of mass may be considered permanent for the time scale of interest. Sorption, therefore, does not permanently remove solute mass from ground water; it merely retards migration. It is this slowing of contaminant migration that must be understood in order to effectively predict the fate of a dissolved contaminant. This section provides information on how retardation coefficients are determined in the laboratory. It is not the intent of this document to instruct people in how to perform these experiments; this information is provided for informational purposes only. Linear isotherms and previously determined soil sorption coefficients (K_{oc}) are generally used to estimate sorption and retardation.

B.2.3.1 Mechanisms of Sorption

Sorption of dissolved contaminants is a complex phenomenon caused by several mechanisms, including London-van der Waals forces, Coulomb forces, hydrogen bonding, ligand exchange, chemisorption (covalent bonding between chemical and aquifer matrix), dipole-dipole forces, dipole-induced dipole forces, and hydrophobic forces. Because of their nonpolar molecular structure, hydrocarbons most commonly exhibit sorption through the process of hydrophobic bonding. When

the surfaces comprising the aquifer matrix are less polar than the water molecule, as is generally the case, there is a strong tendency for the nonpolar contaminant molecules to partition from the ground water and sorb to the aquifer matrix. This phenomenon is referred to as hydrophobic bonding and is an important factor controlling the fate of many organic pollutants in soils (Devinny *et al.*, 1990). Two components of an aquifer have the greatest effect on sorption: organic matter and clay minerals. In most aquifers, the organic fraction tends to control the sorption of organic contaminants.

B.2.3.2 Sorption Models and Isotherms

Regardless of the sorption mechanism, it is possible to determine the amount of sorption to be expected when a given dissolved contaminant interacts with the materials comprising the aquifer matrix. Bench-scale experiments are performed by mixing water-contaminant solutions of various concentrations with aquifer materials containing various amounts of organic carbon and clay minerals. The solutions are then sealed with no headspace and left until equilibrium between the various phases is reached. The amount of contaminant left in solution is then measured.

Both environmental conservative isotherms (ECI) and constant soil to solution isotherms (CSI) can be generated. The ECI study uses the same water concentration but changes the soil to water ratio. In CSI isotherm studies, the concentration of contaminant in water is varied while the amount of water and sediment is constant. In some instances, actual contaminated water from the site is added. Typically, the samples are continually rotated and concentrations measured with time to document equilibrium. True equilibrium may require hundreds of hours of incubation but 80 to 90 percent of equilibrium may be achieved in one or two days.

The results are commonly expressed as a plot of the concentration of chemical sorbed (µg/g) versus the concentration remaining in solution (µg/L). The relationship between the concentration of chemical sorbed (C_a) and the concentration remaining in solution (C_l) at equilibrium is referred to as the sorption isotherm because the experiments are performed at constant temperature.

Sorption isotherms generally exhibit one of three characteristic shapes depending on the sorption mechanism. These isotherms are referred to as the Langmuir isotherm, the Freundlich isotherm, and the linear isotherm (a special case of the Freundlich isotherm). Each of these sorption isotherms, and related equations, are discussed in the following sections.

B.2.3.2.1 Langmuir Sorption Model

The Langmuir model describes sorption in solute transport systems wherein the sorbed concentration increases linearly with increasing solute concentration at low concentrations and approaches a constant value at high concentrations. The sorbed concentration approaches a constant value because there are a limited number of sites on the aquifer matrix available for contaminant sorption. This relationship is illustrated in Figure B.2.10. The Langmuir equation is described mathematically as (Devinny *et al.*, 1990):

$$C_a = \frac{KC_t b}{1 + KC_t} \qquad \text{eq. B.2.10}$$

Where:

C_a = sorbed contaminant concentration (mass contaminant/mass soil)
K = equilibrium constant for the sorption reaction (µg/g)
C_l = dissolved contaminant concentration (µg/ml)
b = number of sorption sites (maximum amount of sorbed contaminant)

The Langmuir model is appropriate for highly specific sorption mechanisms where there are a limited number of sorption sites. This model predicts a rapid increase in the amount of sorbed contaminant as contaminant concentrations increase in a previously pristine area. As sorption sites become filled, the amount of sorbed contaminant reaches a maximum level equal to the number of sorption sites, *b*.

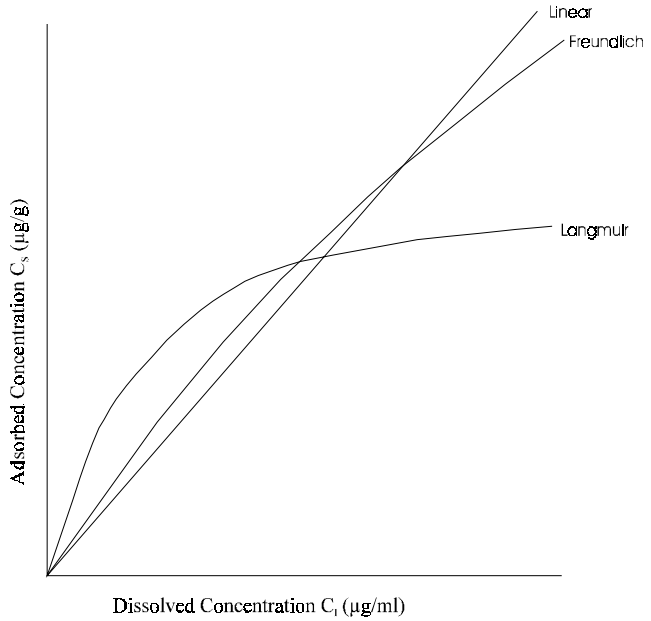

Figure B.2.10 *Characteristic adsorption isotherm shapes.*

B.2.3.2.2 Freundlich Sorption Model

The Langmuir isotherm model can be modified if the number of sorption sites is large (assumed infinite) relative to the number of contaminant molecules. This is generally a valid assumption for dilute solutions (e.g., downgradient from a petroleum hydrocarbon spill in the dissolved BTEX plume) where the number of unoccupied sorption sites is large relative to contaminant concentrations. The Freundlich model is expressed mathematically as (Devinny *et al.*, 1990):

$$C_a = K_d C_l^{1/n} \qquad \text{eq. B.2.11}$$

Where:

K_d = distribution coefficient
C_a = sorbed contaminant concentration (mass contaminant/mass soil, mg/g)
C_l = dissolved concentration (mass contaminant/volume solution, (mg/ml)
n = chemical-specific coefficient

The value of n in this equation is a chemical-specific quantity that is determined experimentally. Values of 1/n typically range from 0.7 to 1.1, but may be as low as 0.3 and as high as 1.7 (Lyman *et al.* 1992).

The simplest expression of equilibrium sorption is the linear sorption isotherm, a special form of the Freundlich isotherm that occurs when the value of n is 1. The linear isotherm is valid for a dissolved species that is present at a concentration less than one half of its solubility (Lyman *et al*., 1992). This is a valid assumption for BTEX compounds partitioning from fuel mixtures into ground water. Dissolved BTEX concentrations resulting from this type of partitioning are significantly less than the pure compound's solubility in pure water. The linear sorption isotherm is expressed as (Jury *et al*., 1991):

$$C_a = K_d C_l \qquad \text{eq. B.2.12}$$

Where:

K_d = distribution coefficient (slope of the isotherm, ml/g).
C_a = sorbed contaminant concentration (mass contaminant/mass soil, µg/g)
C_l = dissolved contaminant concentration (mass contaminant/volume solution, µg/ml)

The slope of the linear isotherm is the distribution coefficient, K_d.

B.2.3.3 Distribution Coefficient

The most commonly used method for expressing the distribution of an organic compound between the aquifer matrix and the aqueous phase is the distribution coefficient, K_d, which is defined as the ratio of the sorbed contaminant concentration to the dissolved contaminant concentration:

$$K_d = \frac{C_a}{C_l} \qquad \text{eq. B.2.13}$$

Where:

K_d = distribution coefficient (slope of the sorption isotherm, ml/g)
C_a = sorbed concentration (mass contaminant/mass soil or μg/g)
C_l = dissolved concentration (mass contaminant/volume solution or μg/ml)

The transport and partitioning of a contaminant is strongly dependent on the chemical's soil/water distribution coefficient and water solubility. The distribution coefficient is a measure of the sorption/desorption potential and characterizes the tendency of an organic compound to be sorbed to the aquifer matrix. The higher the distribution coefficient, the greater the potential for sorption to the aquifer matrix. The distribution coefficient is the slope of the sorption isotherm at the contaminant concentration of interest. The greater the amount of sorption, the greater the value of K_d. For systems described by a linear isotherm, K_d is a constant. In general terms, the distribution coefficient is controlled by the hydrophobicity of the contaminant and the total surface area of the aquifer matrix available for sorption. Thus, the distribution coefficient for a single compound will vary with the composition of the aquifer matrix. Because of their extremely high specific surface areas (ratio of surface area to volume), the organic carbon and clay mineral fractions of the aquifer matrix generally present the majority of sorption sites in an aquifer.

Based on the research efforts of Ciccioli *et al*. (1980), Karickhoff *et al*. (1979), and Schwarzenbach and Westall (1981), it appears that the primary adsorptive surface for organic chemicals is the organic fraction of the aquifer matrix. However, there is a "critical level of organic matter" below which sorption onto mineral surfaces is the dominant sorption mechanism (McCarty *et al*., 1981). The critical level of organic matter, below which sorption appears to be dominated by mineral-solute interactions, and above which sorption is dominated by organic carbon-solute interactions, is given by (McCarty *et al*., 1981):

$$f_{oc_c} = \frac{A_s}{200} \frac{1}{K_{ow}^{0.84}} \qquad \text{eq. B.2.14}$$

Where:

f_{oc_c} = critical level of organic matter (mass fraction)
A_s = surface area of mineralogical component of the aquifer matrix (m^2/g)
K_{ow} = octanol-water partitioning coefficient

From this relationship, it is apparent that the total organic carbon content of the aquifer matrix is less important for solutes with low octanol-water partitioning coefficients (K_{ow}). Also apparent is the fact that the critical level of organic matter increases as the surface area of the mineralogic fraction of the aquifer matrix increases. The surface area of the mineralogic component of the aquifer matrix is most strongly influenced by the amount of clay. For compounds with low K_{ow} values in materials with a high clay content, sorption to mineral surfaces could be an important factor causing retardation of the chemical.

Several researchers have found that if the distribution coefficient is normalized relative to the aquifer matrix total organic carbon content, much of the variation in observed K_d values between different soils is eliminated (Dragun, 1988). Distribution coefficients normalized to total organic carbon content are expressed as K_{oc}. The following equation gives the expression relating K_d to K_{oc}:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad \text{eq. B.2.15}$$

Where:

K_{oc} = soil sorption coefficient normalized for total organic carbon content
K_d = distribution coefficient
f_{oc} = fraction total organic carbon (mg organic carbon/mg soil)

In areas with high clay concentrations and low total organic carbon concentrations, the clay minerals become the dominant sorption sites. Under these conditions, the use of K_{oc} to compute K_d might result in underestimating the importance of sorption in retardation calculations, a source of error that will make retardation calculations based on the total organic carbon content of the aquifer matrix more conservative. In fact, aquifers that have a high enough hydraulic conductivity to spread hydrocarbon contamination generally have low clay content. In these cases, the contribution of sorption to mineral surfaces is generally trivial.

Earlier investigations reported distribution coefficients normalized to total organic matter content (K_{om}). The relationship between f_{om} and f_{oc} is nearly constant and, assuming that the organic matter contains approximately 58 percent carbon (Lyman *et al.*, 1992):

$$K_{oc} = 1.724 K_{om} \qquad \text{eq. B.2.16}$$

B.2.3.4 Coefficient of Retardation

As mentioned earlier, sorption tends to slow the transport velocity of contaminants dissolved in ground water. The coefficient of retardation, R, is used to estimate the retarded contaminant velocity. The coefficient of retardation for linear sorption is determined from the distribution coefficient using the relationship:

$$R = 1 + \frac{\rho_b K_d}{n} \qquad \text{eq. B.2.17}$$

Where:

R = coefficient of retardation [dimensionless]
ρ_b = bulk density of aquifer [M/L^3]
K_d = distribution coefficient [L^3/M]
n = porosity [L^3/L^3]

The retarded contaminant transport velocity, v_c, is given by:

$$v_c = \frac{v_x}{R} \qquad \text{eq. B.2.18}$$

Where:

v_c = retarded contaminant transport velocity [L/T]
v_x = advective ground-water velocity [L/T]
R = coefficient of retardation [dimensionless]

Two methods used to quantify the distribution coefficient and amount of sorption (and thus retardation) for a given aquifer/contaminant system are presented below. The first method involves estimating the distribution coefficient by using K_{oc} for the contaminants and the fraction of organic carbon comprising the aquifer matrix. The second method involves conducting batch or column tests to determine the distribution coefficient. Because numerous authors have conducted experiments to determine K_{oc} values for common contaminants, literature values are reliable, and it generally is not necessary to conduct laboratory tests.

B.2.3.4.1 Determining the Coefficient of Retardation using K_{oc}

Batch and column tests have been performed for a wide range of contaminant types and concentrations and aquifer conditions. Numerous studies have been performed using the results of these

tests to determine if relationships exist that are capable of predicting the sorption characteristics of a chemical based on easily measured parameters. The results of these studies indicate that the amount of sorption is strongly dependent on the amount of organic carbon present in the aquifer matrix and the degree of hydrophobicity exhibited by the contaminant (Bailey and White, 1970; Karickhoff *et al*., 1979; Kenaga and Goring, 1980; Brown and Flagg, 1981; Schwarzenbach and Westall, 1981; Hassett *et al*., 1983; Chiou *et al*., 1983). These researchers observed that the distribution coefficient, K_d, was proportional to the organic carbon fraction of the aquifer times a proportionality constant. This proportionality constant, K_{oc}, is defined as given by equation B.2.15. In effect, equation B.2.15 normalizes the distribution coefficient to the amount of organic carbon in the aquifer matrix. Because it is normalized to organic carbon, values of K_{oc} are dependent only on the properties of the compound (not on the type of soil). Values of K_{oc} have been determined for a wide range of chemicals. Table B.2.1 lists K_{oc} values for selected chlorinated compounds, and Table B.2.2 lists K_{oc} values for BTEX and trimethylbenzene.

By knowing the value of K_{oc} for a contaminant and the fraction of organic carbon present in the aquifer, the distribution coefficient can be determined by using the relationship:

$$K_d = K_{oc} f_{oc} \qquad \text{eq. B.2.19}$$

When using the method presented in this section to predict sorption of the BTEX compounds, total organic carbon concentrations obtained from the most transmissive aquifer zone should be averaged and used for predicting sorption. This is because the majority of dissolved contaminant transport occurs in the most transmissive portions of the aquifer. In addition, because the most transmissive aquifer zones generally have the lowest total organic carbon concentrations, the use of this value will give a conservative prediction of contaminant sorption and retardation.

Table B.2.1 *Values of Aqueous Solubility and K_{oc} for Selected Chlorinated Compounds*

Compound	**Solubility (mg/L)**	**K_{oc} (L/Kg)**
Tetrachloroethene	150[a]	263[a]
Tetrachloroethene		359[b]
Tetrachloroethene	1,503[c]	209 - 238[c]
Trichloroethene	1,100[a]	107[a]
Trichloroethene		137[b]
Trichloroethene	1,100[c]	87 - 150[c]
1,1-Dichloroethene	2,250[a]	64.6[a]
1,1-Dichloroethene		80.2[b]
1,1-Dichloroethene	2,500[d]	150[d]
cis-1,2-Dichloroethene		80.2[b]
cis-1,2-Dichloroethene	3,500[c]	49[c]
trans-1,2-Dichloroethene	6,300[a]	58.9[a]
trans-1,2-Dichloroethene		80.2[b]
trans-1,2-Dichloroethene	6,300[c]	36[c]
Vinyl Chloride	1,100[a]	2.45[a]
Vinyl Chloride	2,763[d]	0.4 - 56[d]
1,1,1-Trichloroethane	1,495[c]	183[c]
1,1,2-Trichloroethane	4,420[e]	70[e]
1,1-Dichloroethane	5,060[d]	40[d]
1,2-Dichloroethane	8,520[c]	33 to 152[c]
Chloroethane	5,710[e]	33 to 143[e]
Hexachlorobenzene	0.006[f]	--
1,2-Dichlorobenzene	156[c]	272 - 1480[c]
1,3-Dichlorobenzene	111[g]	293 to 31,600[g]
1,4-Dichlorobenzene	74 to 87[d]	273 to 1833[d]
Chlorobenzene	472[d]	83 to 389[d]
Carbon Tetrachloride	805[g]	110[g]
Chloroform	7,950[c]	<34[c]
Methylene Chloride	13,000[c]	48[c]

[a] *From Knox et al., 1993*
[b] *From Jeng et al., 1992; Temperature = 20°C*
[c] *From Howard, 1990; Temperature = 25°C*
[d] *From Howard, 1989; Temperature = 25°C*
[e] *From Howard, 1989; Temperature = 20°C*
[f] *ATSDR, 1990; Temperature = 20°C*
[g] *From Howard, 1990; Temperature = 20°C*

Table B.2.2 *Values of Aqueous Solubility and K_{oc} for BTEX and Trimethylbenzene Isomers*

Compound	Solubility (mg/L)	K_{oc} (L/Kg)
Benzene	1750[a]	87.1[a]
Benzene		83[b]
Benzene	1780[c]	190[c,d,f]
Benzene	1780[c]	62[c,e,f]
Benzene	1780[h]	72[h,i]
Benzene*	1780[h]	79[h,j,*]
Benzene	1780[c,h]	89[k]
Toluene	515[a]	151[a]
Toluene		303[b]
Toluene	537[c]	380[c,d,f]
Toluene	537[c]	110[c,e,f]
Toluene*	537[c]	190[k,*]
Ethylbenzene	152[a]	158.5[a]
Ethylbenzene		519[b]
Ethylbenzene	167[c]	680[c,d,f]
Ethylbenzene	167[c]	200[c,e,f]
Ethylbenzene	140[h]	501[h,i]
Ethylbenzene*	140[h]	468[h,j]
Ethylbenzene	167[c]	398[k]
o-xylene	152[a]	128.8[a]
o-xylene		519[b]
o-xylene*	152[a]	422[k,*]
m-xylene	158[a]	
m-xylene		519[b]
m-xylene	162[c]	720[c,d,f]
m-xylene	162[c]	210[c,e,f]
m-xylene*	162[c]	405.37[k,*]
p-xylene	198[a]	204[a]
p-xylene		519[b]
p-xylene*	198[a]	357[k,*]
1,2,3-trimethylbenzene*	75	884[b,*]
1,2,4-trimethylbenzene	59[l]	884[b]
1,2,4-trimethylbenzene*	59[l]	772[k,*]
1,3,5-trimethylbenzene*	72.60[g]	676[k,*]

[a] *From Knox et al., 1993*
[b] *From Jeng et al., 1992; Temperature = 20°C*
[c] *From Lyman et al., 1992; Temperature = 25°C*
[d] *Estimated from K_{ow}*
[e] *Estimated from solubility*
[f] *Estimate from solubility generally considered more reliable*
[g] *From Lyman et al., 1992; Temperature = 20°C*
[h] *From Fetter, 1993*
[I] *Average of 12 equations used to estimate K_{oc} from K_{ow} or K_{om}*
[j] *Average of 5 equations used to estimate K_{oc} from Solubility*
[k] *Average using equations from Kenaga and Goring (1980), Means et al. (1980), and Hassett et al. (1983) to estimate K_{oc} from solubility*
[l] *From Sutton and Calder (1975)*
* *Recommended value*

B.2.3.4.2 Determining the Coefficient of Retardation using Laboratory Tests

The distribution coefficient may be quantified in the laboratory using batch or column tests. Batch tests are easier to perform than column tests. Although more difficult to perform, column tests generally produce a more accurate representation of field conditions than batch tests because continuous flow is involved. Knox *et al*. (1993) suggest using batch tests as a preliminary screening tool, followed by column studies to confirm the results of batch testing. The authors of this document feel that batch tests, if conducted properly, will yield sufficiently accurate results for fate and transport modeling purposes provided that sensitivity analyses for retardation are conducted during the modeling.

Batch testing involves adding uncontaminated aquifer material to a number of vessels, adding solutions prepared using uncontaminated ground water from the site mixed with various amounts of contaminants to produce varying solute concentrations, sealing the vessel and shaking it until equilibrium is reached, analyzing the solute concentration remaining in solution, and calculating the amount of contaminant sorbed to the aquifer matrix using mass balance calculations. A plot of the concentration of contaminant sorbed versus dissolved equilibrium concentration is then made using the data for each reaction vessel. The slope of the line formed by connecting each data point is the distribution coefficient. The temperature should be held constant during the batch test, and should approximate that of the aquifer system through which solute transport is taking place.

Table B.2.3 contains data from a hypothetical batch test. These data are plotted (Figure B.2.11) to obtain an isotherm unique to the aquifer conditions at the site. A regression analysis can then be performed on these data to determine the distribution coefficient. For linear isotherms, the distribution coefficient is simply the slope of the isotherm. In this example, K_d = 0.0146 L/g. Batch-testing procedures are described in detail by Roy *et al.* (1992).

Column testing involves placing uncontaminated aquifer matrix material in a laboratory column and passing solutions through the column. Solutions are prepared by mixing uncontaminated ground water from the site with the contaminants of interest and a conservative tracer. Flow rate and time are accounted for and samples are periodically taken from the effluent of the column and analyzed to determine contaminant and tracer concentrations. Breakthrough curves are prepared for the contaminants by plotting chemical concentration versus time (or relative concentration versus number of pore volumes). The simplest way to determine the coefficient of retardation (or the distribution coefficient) from the breakthrough curves is to determine the time required for the effluent concentration to equal 0.5 of the influent concentration. This value can be used to determine average velocity of the center of mass of the contaminant. The retardation factor is determined by dividing the average flow velocity through the column by the velocity of the center of mass of the contaminant. The value thus obtained is the retardation factor. The coefficient of retardation also can be determined by curve fitting using the CXTFIT model of Parker and van Genuchten (1984). Breakthrough curves also can be made for the conservative tracer. These curves can be used to determine the coefficient of dispersion by curve fitting using the model of Parker and van Genuchten (1984).

When using the method presented in this section to predict sorption of the BTEX compounds, aquifer samples should be obtained from the most transmissive aquifer zone. This is because the majority of dissolved contaminant transport occurs in the most transmissive portions of the aquifer. In addition, because the most transmissive aquifer zones generally have the lowest organic carbon concentrations, the use of these materials will give a conservative prediction of contaminant sorption and retardation.

Table B.2.3 *Data from Hypothetical Batch Test Experiment*

Initial Concentration (µg/L)	Equilibrium Concentration (µg/L)	Weight of Solid Matrix (g)	Sorbed Concentration* (µg/g)
250	77.3	20.42	1.69
500	150.57	20.42	3.42
1000	297.04	20.42	6.89
1500	510.1	20.42	9.70
2000	603.05	20.42	13.68
3800	1198.7	20.42	25.48
6000	2300.5	20.42	36.23
9000	3560.7	20.42	53.27

* *Adsorbed concentration = ((Initial concentration - Equilibrium Concentration) x Volume of Solution) / Weight of Solid Matrix*

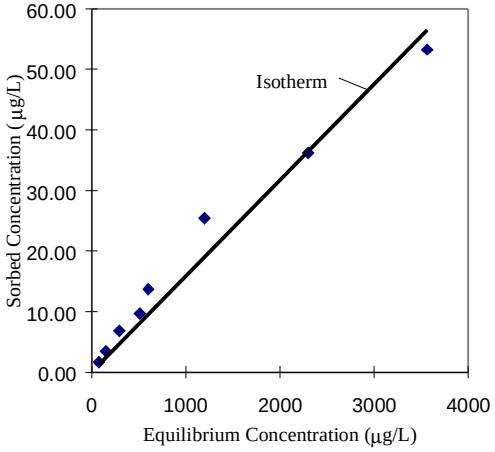

Figure B.2.11 *Plot of sorbed concentration vs. equilibrium concentration.*

B.2.3.5 One-Dimensional Advection-Dispersion Equation with Retardation

The advection-dispersion equation is obtained by adding hydrodynamic dispersion to equation B.2.2. In one dimension, the advection-dispersion equation is given by:

$$R\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \qquad \text{eq. B.2.20}$$

Where:

v_x = average linear velocity ground-water velocity [L/T]
R = coefficient of retardation [dimensionless]
C = contaminant concentration [M/L^3]
D_x = hydrodynamic dispersion [L^2/T]
t = time [T]
x = distance along flow path [L]

This equation considers advection, hydrodynamic dispersion, and sorption (retardation). Because of biodegradation, this equation generally must be combined with the other components of the modified advection-dispersion equation, presented as equation B.1.1, to obtain an accurate mathematical description of solute transport.

B.2.4 VOLATILIZATION

While not a destructive attenuation mechanism, volatilization does remove contaminants from the ground-water system. In general, factors affecting the volatilization of contaminants from ground water into soil gas include the contaminant concentration, the change in contaminant concentration with depth, the Henry's Law constant and diffusion coefficient of the compound, mass transport coefficients for the contaminant in both water and soil gas, sorption, and the temperature of the water (Larson and Weber, 1994).

Partitioning of a contaminant between the liquid phase and the gaseous phase is governed by Henry's Law. Thus, the Henry's Law constant of a chemical determines the tendency of a contaminant to volatilize from ground water into the soil gas. Henry's Law states that the concentration of a contaminant in the gaseous phase is directly proportional to the compound's concentration in the liquid phase and is a constant characteristic of the compound. Stated mathematically, Henry's Law is given by (Lyman *et al.,* 1992):

$$C_a = HC_l \qquad \text{eq. B.2.21}$$

Where:

H = Henry's Law Constant (atm m^3/mol)
C_a = concentration in air (atm)
C_l = concentration in water (mol/m^3)

Henry's Law constants for chlorinated and petroleum hydrocarbons range over several orders of magnitude. For petroleum hydrocarbons, Henry's Law constants (H) for the saturated aliphatics, H range from 1 to 10 atm m^3/mol @ 25°C; for the unsaturated and cyclo-aliphatics ranges from 0.1 to 1 atm m^3/mol @ 25°C; and for the light aromatics (e.g., BTEX) H ranges from 0.007 to 0.02 atm m^3/mol @ 25°C (Lyman *et al*., 1992). Values of Henry's Law constants for selected chlorinated solvents and the BTEX compounds are given in Table B.2.4. As indicated on the table, values of H for chlorinated compounds also vary over several orders of magnitude, although most are similar to those for BTEX compounds.

The physiochemical properties of chlorinated solvents and the BTEX compounds give them low Henry's Law constants, with the exception of vinyl chloride. Because of the small surface area of the ground-water flow system exposed to soil gas, volatilization of chlorinated solvents and BTEX compounds from ground water is a relatively slow process that, in the interest of being conservative, generally can be neglected when modeling biodegradation. Chiang *et al.* (1989) demonstrated that less than 5 percent of the mass of dissolved BTEX is lost to volatilization in the saturated ground-water environment. Moreover, Rivett (1995) observed that for plumes more than about 1 meter below the air-water interface, little, if any, solvent concentrations will be detectable in soil gas due to the downward ground-water velocity in the vicinity of the water table. This suggests that for portions of plumes more than 1 meter below the water table, very little, if any, mass will be lost due to volatilization. In addition, vapor transport across the capillary fringe can be very slow (McCarthy and Johnson, 1993), thus further limiting mass transfer rates. Because of this, the impact of volatilization on dissolved contaminant reduction can generally be neglected, except possibly in the case of vinyl chloride. However, Rivett's (1995) findings should be kept in mind even when considering volatilization as a mechanism for removal of vinyl chloride from ground water.

B.2.5 RECHARGE

Groundwater recharge can be defined as the entry into the saturated zone of water made available at the water-table surface (Freeze and Cherry, 1979). In recharge areas, flow near the water table is generally downward. Recharge defined in this manner may therefore include not only precipitation that infiltrates through the vadose zone, but water entering the ground-water system due to discharge from surface water bodies (i.e., streams and lakes). Where a surface water body is in

Table B.2.4 *Henry's Law Constants and Vapor Pressures for Common Fuel Hydrocarbons and Chlorinated Solvents*

Compound	**Vapor Pressure (mmHg @ 25°C)**	**Henry's Law Constant (atm-m^3/mol)**
Benzene	95	0.0054
Ethylbenzene	10	0.0066
Toluene	28.4	0.0067
o-Xylene	10	0.00527
m-Xylene	10	0.007
p-Xylene	10	0.0071
1,2,3-Trimethylbenzene		0.00318
1,2,4-Trimethylbenzene		0.007
1,3,5-Trimethylbenzene		0.006
1,2,4,5-Tetramethylbenzene		0.0249
Tetrachloroethene	14	0.0153
Trichloroethene	57.8	0.0091
1,1-Dichloroethene	591	0.018
cis-1,2-Dichloroethene	200	0.0037
trans-1,2-Dichloroethene	265	0.0072
Vinyl Chloride	2,580	1.22
1,1,1-Trichloroethane	123.7	0.008
1,1,2-Trichloroethane	30.3	0.0012
1,1-Dichloroethane	227	0.0059
1,2-Dichloroethane	78.7	0.00098
Chloroethane	766	0.0085
Hexachlorobenzene	0.0000109	0.00068
1,2-Dichlorobenzene	1.47	0.0012
1,3-Dichlorobenzene	2.3	0.0018
1,4-Dichlorobenzene	1.76	0.0015
Chlorobenzene	11.9	0.0035
Carbon Tetrachloride	113.8	0.0304
Chloroform	246	0.00435
Methylene Chloride	434.9	0.00268

contact with or is part of the ground-water system, the definition of recharge above is stretched slightly. However, such bodies are often referred to as recharging lakes or streams. Recharge of a water table aquifer has two effects on the natural attenuation of a dissolved contaminant plume. Additional water entering the system due to infiltration of precipitation or from surface water will contribute to dilution of the plume, and the influx of relatively fresh, electron-acceptor-charged water will alter geochemical processes and in some cases facilitate additional biodegradation.

Recharge from infiltrating precipitation is the result of a complex series of processes in the unsaturated zone. Description of these processes is beyond the scope of this discussion; however, it is worth noting that the infiltration of precipitation through the vadose zone brings the water into contact with the soil and thus may allow dissolution of additional electron acceptors and possibly organic soil matter (a potential source of electron donors). Infiltration, therefore, provides fluxes of water, inorganic species, and possibly organic species into the ground water. Recharge from surface water bodies occurs when the hydraulic head of the body is greater than that of the adjacent ground water. The surface water may be a connected part of the ground-water system, or it may be perched above the water table. In either case, the water entering the ground-water system will not only aid in dilution of a contaminant plume but it may also add electron acceptors and possibly electron donors to the ground water.

An influx of electron acceptors will tend to increase the overall electron-accepting capacity within the contaminant plume. In addition to the inorganic electron acceptors that may be dissolved in the recharge (e.g., dissolved oxygen, nitrate, or sulfate), the introduction of water with different geochemical properties may foster geochemical changes in the aquifer. For example, iron (II) will be oxidized back to iron (III). Vroblesky and Chapelle (1994) present data from a site where a major rainfall event introduced sufficient dissolved oxygen into the contaminated zone to cause reprecipitation of iron (III) onto mineral grains. This reprecipitation made iron (III) available for reduction by microorganisms, thus resulting in a shift from methanogenesis back to iron (III) reduction (Vroblesky and Chapelle, 1994). Such a shift may be beneficial for biodegradation of compounds used as electron donors, such as fuel hydrocarbons or vinyl chloride. However, these shifts can also make conditions less favorable for reductive dehalogenation.

Evaluating the effects of recharge is typically difficult. The effects of dilution might be estimated if one has a detailed water budget for the system in question, but if a plume has a significant vertical extent, it cannot be known with any certainty what proportion of the plume mass is being diluted by the recharge. Moreover, because dispersivity, sorption, and biodegradation are often not well-quantified, separating out the effects of dilution may be very difficult indeed. Where recharge enters from precipitation, the effects of the addition of electron acceptors may be qualitatively apparent due to elevated electron acceptor concentrations or differing patterns in electron acceptor consumption or byproduct formation in the area of the recharge. However, the effects of short-term variations in such a system (which are likely due to the intermittent nature of precipitation events in most climates) may not be easily understood. Where recharge enters from surface water, the influx of mass and electron acceptors is more steady over time. Quantifying the effects of dilution may be less uncertain, and the effects of electron acceptor replenishment may be more easily identified (though not necessarily quantified).

SECTION B-3
DESTRUCTIVE ATTENUATION MECHANISMS - BIOLOGICAL

Many anthropogenic organic compounds, including certain chlorinated solvents, can be degraded by both biological and abiotic mechanisms. Biological degradation mechanisms are discussed in this section; abiotic degradation mechanisms are discussed in Section B.4. Table B.3.1 summarizes the various biotic and abiotic mechanisms that result in the degradation of anthropogenic organic compounds. Biological degradation mechanisms tend to dominate in most groundwater systems, depending on the type of contaminant and the ground-water chemistry.

Table B.3.1 *Biologic and Abiotic Degradation Mechanisms for Various Anthropogenic Organic Compounds*

Compound	Degradation Mechanism
PCE	Reductive dechlorination
TCE	Reductive dechlorination, cometabolism
DCE	Reductive dechlorination, direct biological oxidation
Vinyl Chloride	Reductive dechlorination, direct biological oxidation
TCA	Reductive dechlorination, hydrolysis, dehydrohalogenation
1,2-DCA	Reductive dechlorination, direct biological oxidation
Chloroethane	Hydrolysis
Carbon Tetrachloride	Reductive dechlorination, cometabolism, abiotic
Chloroform	Reductive dechlorination, cometabolism
Methylene Chloride	Direct biological oxidation
Chlorobenzenes	Direct biological oxidation, reductive dechlorination, cometabolism
Benzene	Direct biological oxidation
Toluene	Direct biological oxidation
Ethylbenzene	Direct biological oxidation
Xylenes	Direct biological oxidation
1,2-Dibromoethane	Reductive dehalogenation, hydrolysis, direct biological oxidation

Many organic contaminants are biodegraded by microorganisms indigenous to the subsurface environment. During biodegradation, dissolved contaminants are ultimately transformed into innocuous byproducts such as carbon dioxide, chloride, methane, and water. In some cases, intermediate products of these transformations may be more hazardous than the original compound; however, they may also be more easily degraded. Biodegradation of organic compounds dissolved in ground water results in a reduction in contaminant concentration (and mass) and slowing of the contaminant front relative to the average advective ground-water flow velocity. Figures B.3.1 and B.3.2 illustrate the effects of biodegradation on an advancing solute front.

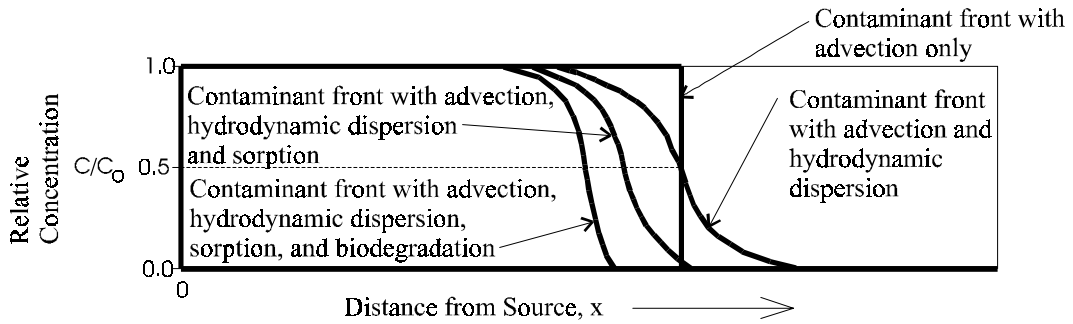

Figure B.3.1 *Breakthrough curve in one dimension showing plug flow with continuous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; the combined processes of advection, hydrodynamic dispersion, and sorption; and the combined processes of advection, hydrodynamic dispersion, sorption, and biodegradation.*

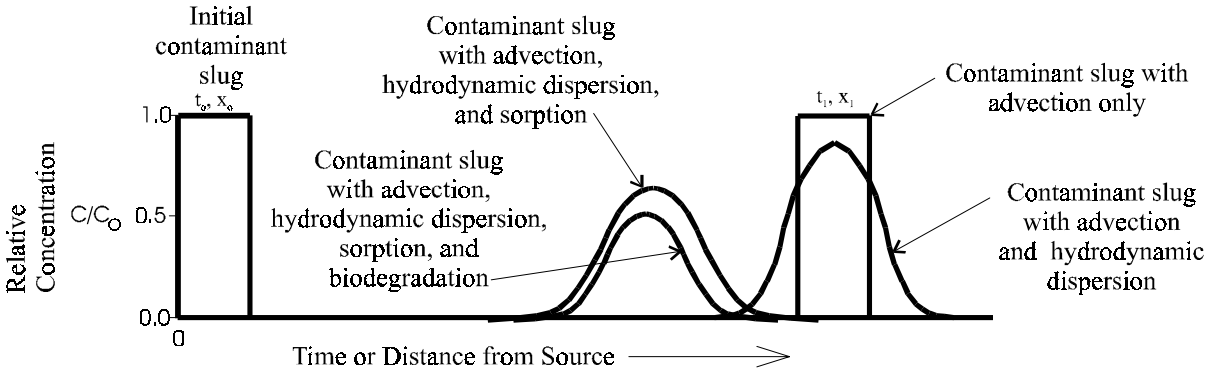

Figure B.3.2 *Breakthrough curve in one dimension showing plug flow with instantaneous source resulting from advection only; the combined processes of advection and hydrodynamic dispersion; the combined processes of advection, hydrodynamic dispersion, and sorption; and the combined processes of advection, hydrodynamic dispersion, sorption, and biodegradation.*

B.3.1 OVERVIEW OF BIODEGRADATION

As recently as 1975 the scientific literature reported the subsurface/aquifer environment as devoid of significant biological activity. It is now known that soils and shallow sediments contain a large variety of microorganisms, ranging from simple prokaryotic bacteria and cyanobacteria to more complex eukaryotic algae, fungi, and protozoa. Over the past two decades, numerous laboratory and field studies have shown that microorganisms indigenous to the subsurface environment can degrade a variety of organic compounds, including components of gasoline, kerosene, diesel, jet fuel, chlorinated ethenes, chlorinated ethanes, the chlorobenzenes, and many other compounds (e.g., for fuels see Jamison *et al.*, 1975; Atlas, 1981, 1984, and 1988; Young, 1984; Bartha, 1986; B. H. Wilson *et al.*, 1986 and 1990; Barker *et al.*, 1987; Baedecker *et al.*, 1988; Lee, 1988; Chiang *et al.*, 1989; Cozzarelli *et al.*, 1990; Leahy and Colewell, 1990; Alvarez and Vogel, 1991; Evans *et al.*, 1991a and 1991b; Edwards *et al.*, 1992; Edwards and Grbic-Galic, 1992; Thierrin *et al.*, 1992; Malone *et al.*, 1993; Davis *et al.*, 1994a and 1994b; and Lovley *et al.*, 1995; and for chlorinated solvents see Brunner and Leisinger, 1978; Brunner *et al.*, 1980; Rittman and McCarty, 1980; Bouwer *et al.*, 1981;

Table B.3.2 *Some Microorganisms Capable of Degrading Organic Compounds(Modified from Riser-Roberts, 1992)*

Contaminant	**Microorganisms**	**Comments/ Biodegradability**
Benzene	*Pseudomonas putida, P. rhodochrous, P. aeruginosa, Acinetobacter sp., Methylosinus trichosporium* OB3b, *Nocardia sp., methanogens, anaerobes*	Moderate to High
Toluene	*Methylosinus trichosporium* OB3b, *Bacillus sp., Pseudomonas sp., P. putida, Cunninghamella elegans, P. aeruginosa, P. mildenberger, P. aeruginosa, Achromobacter sp., methanogens, anaerobes*	High
Ethylbenzene	*Pseudomonas putida*	High
Xylenes	*Pseudomonas putida, methanogens, anaerobes*	High
Jet Fuels	*Cladosporium, Hormodendrum*	High
Kerosene	*Torulopsis, Candidatropicalis, Corynebacterium hydrocarboclastus, Candidaparapsilosis, C. guilliermondii, C. lipolytica, Trichosporon sp., Rhohosporidium toruloides, Cladosporium resinae*	High
Chlorinated Ethenes	*Dehalobacter restrictus, Dehalospirillum multivorans, Enterobacter agglomerans, Dehalococcus entheogenes* strain 195,*Desulfitobacterium sp.* strain PCE1, *Pseudomonas putida* (multiple strains), *P. cepacia* G4, *P. mendocina, Desulfobacterium sp., Methanobacterium sp., Methanosarcina sp.* strain DCM, *Alcaligenes eutrophus* JMP 134, *Methylosinus trichosporium OB3b, Escherichia coli, Nitorsomonas europaea, Methylocystis parvus* OBBP, *Mycobacterium sp., Rhodococcus erythopolis*	Moderate
Chlorinated Ethanes	*Desulfobacterium sp., Methanobacterium sp., Pseudomonas putida, Clostridium sp., C. sp.* strain TCAIIB,	Moderate
Chlorinated Methanes	*Acetobacterium woodii, Desulfobacterium sp., Methanobacterium sp., Pseudomonas sp.* strain KC, *Escherichia coli* K-12, *Clostridium sp., Methanosarcina sp., Hyphomicrobium sp.* strain DM2,	Moderate
Chlorobenzenes	*Alcaligenes sp.* (multiple strains), *Pseudomonas sp.*(multiple strains*), P. putida, Staphylococcus epidermis*	Moderate to High

Miller and Guengerich, 1982; Roberts *et al*., 1982; Bouwer and McCarty, 1983; Stucki *et al*., 1983; Reineke and Knackmuss, 1984; Wilson and Wilson, 1985; Fogel *et al*., 1986; Egli *et al*., 1987; Vogel and McCarty, 1987; Vogel *et al*., 1987; Bouwer and Wright, 1988; Little *et al*., 1988; Freedman and Gossett, 1989; Sewell and Gibson, 1991; Chapelle, 1993; DeBruin *et al*., 1992; Ramanand *et al*., 1993; Vogel, 1994; Suflita and Townsend, 1995; Adriaens and Vogel, 1995; Bradley and Chapelle, 1996; Gossett and Zinder, 1996; Spain, 1996). Table B.3.2 presents a partial list of microorganisms known to degrade anthropogenic organic compounds.

Although we now recognize that microorganisms are ubiquitous in drinking water aquifers, the study of the microbial ecology and physiology of the subsurface, below the rhizosphere, is still in its infancy. However, great progress has been made at least in identifying, if not fully understanding,

the numerous and diverse types of microbially-mediated contaminant transformations that can occur in the subsurface.

Chemothrophic organisms, such as humans and most microorganisms, obtain energy for growth and activity from physiologically coupling oxidation and reduction reactions and harvesting the chemical energy that is available. Under aerobic conditions (in the presence of molecular oxygen) humans and many bacteria couple the oxidation of organic compounds (food) to the reduction of oxygen (from the air). However in the absence of oxygen (anaerobic conditions), microorganisms may use other compounds as electron acceptors. Anaerobic microorganisms can obtain energy from a variety of electron donors such as natural organic carbon or many forms of anthropogenic carbon and electron acceptors such as nitrate, iron (III), sulfate, carbon dioxide, as well as many of the chlorinated solvents.

The introduction of oxidizable soluble organic contaminants into ground water initiates a series of complex responses by subsurface microorganisms. Field and laboratory research suggests that distinct communities defined by the dominant electron acceptor develop which are spatially and temporally separate. These communities are most likely ecologically defined by the flux of biologically available electron donors and acceptors. The biological processes of these communities are potentially useful as natural attenuation mechanisms, as the basis of new bioremediation technologies, and as indicators of the extent and severity of the release. As electron acceptors and nutrients are depleted by microbial activity during biodegradation of contaminants, the redox potential of contaminated aquifers decreases. This results in a succession of bacterial types adapted to specific redox regimes and electron acceptors. Metabolic byproducts of contaminant biodegradation also exert selective forces, either by presenting different carbon sources or by further modifying the physical and chemical environment of the aquifer. Like organic and inorganic colloids, microorganisms possess complex surface chemistry, and can themselves serve as mobile and immobile reactive sites for contaminants.

Under anaerobic conditions, most organic compounds are degraded by groups of interacting microorganisms referred to as a consortium. In the consortium, individual types of organisms carry out different specialized reactions which, when combined, can lead to the complete mineralization of a particular compound. The metabolic interaction between organisms can be complex and may be so tightly linked under a given set of conditions that stable consortia can be mistakenly identified as a single species. There seems to be several advantages to the consortial system, including: 1) This system allows for the creation of microenvironments where certain types of organisms can survive in otherwise hostile conditions; 2) Reactions that are thermodynamically unfavorable can be driven by favorable reactions when they are metabolically linked within the consortium; and, 3) This system takes advantage of the diverse metabolic capabilities of microorganisms by allowing for the formation and enrichment of associations that can utilize an introduced substrate faster than a single species could evolve a novel complex enzyme pathway to degrade the same compound.

It appears that subsurface microbial communities contain the metabolic diversity required to utilize a wide variety of organic contaminants as a primary growth substrate in the presence of electron acceptors such as oxygen. Some pollutants, especially the highly oxidized chlorinated hydrocarbons, are not amenable to use as a primary growth substrate. Instead, these compounds are used as electron acceptors in reactions that rely on another source of carbon as a primary substrate or are degraded fortuitously via cometabolism. Thus, biodegradation of organic compounds in ground water occurs via three mechanisms:

- Use of the organic compound as the primary growth substrate;
- Use of the organic compound as an electron acceptor; and
- Cometabolism.

The first two biodegradation mechanisms involve the microbial transfer of electrons from electron donors (primary growth substrate) to electron acceptors. This process can occur under aerobic or anaerobic conditions. Electron donors include natural organic material, fuel hydrocarbons, chlorobenzenes, and the less oxidized chlorinated ethenes and ethanes. Electron acceptors are elements or compounds that occur in relatively oxidized states. The most common naturally occurring electron acceptors in ground water include dissolved oxygen, nitrate, manganese (IV), iron (III), sulfate, and carbon dioxide. In addition, the more oxidized chlorinated solvents such as PCE, TCE, DCE, TCA, DCA, and polychlorinated benzenes can act as electron acceptors under favorable conditions. Under aerobic conditions, dissolved oxygen is used as the terminal electron acceptor during aerobic respiration. Under anaerobic conditions, the electron acceptors listed above are used during denitrification, manganese (IV) reduction, iron (III) reduction, sulfate reduction, methanogenesis, or reductive dechlorination. Chapelle (1993) and Atlas (1988) discuss terminal electron accepting processes in detail.

The third biodegradation mechanism is cometabolism. During cometabolism the compound being degraded does not benefit the organism. Instead, degradation is brought about by a fortuitous reaction wherein an enzyme produced during an unrelated reaction degrades the organic compound.

As discussed in sections B.3.2, B.3.3, and B.3.4, biodegradation causes measurable changes in ground-water chemistry. Table B.3.3 summarizes these trends. During aerobic respiration, oxygen is reduced to water, and dissolved oxygen concentrations decrease. In anaerobic systems where nitrate is the electron acceptor, the nitrate is reduced to NO_2^-, N_2O, NO, NH^{4+}, or N_2 via denitrification or dissimilatory nitrate reduction, nitrate concentrations decrease. In anaerobic systems where iron (III) is the electron acceptor, it is reduced to iron (II) via iron (III) reduction, and iron (II) concentrations increase. In anaerobic systems where sulfate is the electron acceptor, it is reduced to H_2S via sulfate reduction, and sulfate concentrations decrease. During aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction, total alkalinity will increase. In anaerobic systems where CO_2 is used as an electron acceptor, it is reduced by methanogenic bacteria during methanogenesis, and CH_4 is produced. In anaerobic systems where contaminants are being used as electron acceptors, they are reduced to less chlorinated daughter products; in such a system, parent compound concentrations will decrease and daughter product concentrations will increase at first and then decrease as the daughter product is used as an electron acceptor or is oxidized.

As each subsequent electron acceptor is utilized, the ground water becomes more reducing and the redox potential of the water decreases. Figure B.3.3 shows the typical ORP conditions for ground water when different electron acceptors are used. The main force driving this change in ORP is microbially mediated oxidation-reduction reactions. ORP can be used as a crude indicator of which oxidation-reduction reactions may be operating at a site. The ORP determined in the field using an electrode is termed Eh. Eh can be expressed as pE, which is the hypothetical measure of the electron activity associated with a specific Eh. High pE means that the solution or redox couple has a relatively high oxidizing potential.

B.3.2 BIODEGRADATION OF ORGANIC COMPOUNDS VIA USE AS A PRIMARY GROWTH SUBSTRATE

Many organic compounds including natural organic carbon, fuel hydrocarbons, and the less oxidized chlorinated compounds such as DCE, 1,2-DCA, chlorobenzene, or vinyl chloride can be used as primary growth substrates (electron donor) for microbial metabolism. The following sections describe biodegradation of organic compounds through use as a primary substrate under both aerobic and anaerobic conditions.

B.3.2.1 Aerobic Biodegradation of Primary Substrates

Biodegradation of organic compounds is often an aerobic process that occurs when indigenous populations of microorganisms are supplied with the oxygen and nutrients necessary to utilize

Table B.3.3 *Trends in Contaminant, Electron Acceptor, Metabolic By-product and Total Alkalinity Concentrations During Biodegradation*

Analyte	Terminal Electron Accepting Process	Trend in Analyte Concentration During Biodegradation
Fuel Hydrocarbons	Aerobic Respiration, Denitrification, Manganese (IV) Reduction, Iron (III) Reduction, Methanogenesis	Decreases
Highly Chlorinated Solvents and Daughter Products	Reductive Dechlorination	Parent Compound Concentration Decreases, Daughter Products Increase Initially and Then May Decrease
Lightly Chlorinated Solvents	Aerobic Respiration, Denitrification, Manganese (IV) Reduction, Iron (III) Reduction (Direct Oxidation)	Compound Concentration Decreases
Dissolved Oxygen	Aerobic Respiration	Decreases
Nitrate	Denitrification	Decreases
Manganese (II)	Manganese (IV) Reduction	Increases
Iron (II)	Iron (III) Reduction	Increases
Sulfate	Sulfate Reduction	Decreases
Methane	Methanogenesis	Increases
Chloride	Reductive Dechlorination or Direct Oxidation of Chlorinated Compound	Increases
ORP	Aerobic Respiration, Denitrification, Manganese (IV) Reduction, Iron (III) Reduction, Methanogenesis	Decreases
Alkalinity	Aerobic Respiration, Denitrification, Iron (III) Reduction, and Sulfate Reduction	Increases

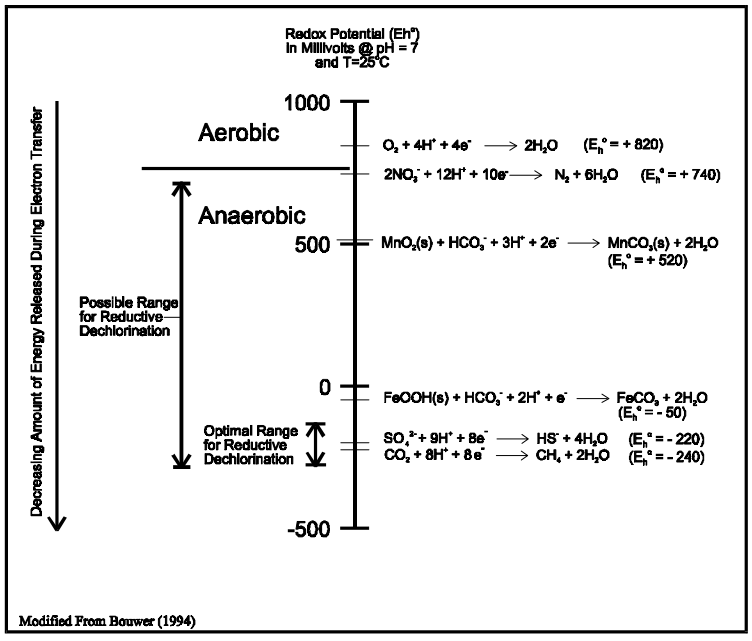

Figure B.3.3 *Oxidation-reduction potentials for various oxidation-reduction reactions.*

organic carbon as an energy source. The biodegradation of fuel hydrocarbons occurs rapidly under aerobic conditions and is discussed in Wiedemeier *et al.* (1995a). Some pollutants, especially the highly oxidized chlorinated hydrocarbons (i.e., those containing more chlorine substituents), are biologically recalcitrant under aerobic conditions. However, some of the less chlorinated ethenes and ethanes such as DCE, VC, and 1,2-DCA, and many of the chlorinated benzenes can be utilized as primary substrates and oxidized under aerobic conditions. During aerobic biodegradation (oxidation) of chlorinated solvents, the facilitating microorganism obtains energy and organic carbon from the degraded solvent.

Of the chlorinated ethenes, vinyl chloride is the most susceptible to aerobic biodegradation, and PCE the least. Of the chlorinated ethanes, 1,2-DCA is the most susceptible to aerobic biodegradation (chloroethane is more likely to abiotically hydrolyze to ethanol), while TCA, tetrachloroethane, and hexachloroethane are less so. Chlorinated benzenes with up to 4 chlorine atoms (i.e., chlorobenzene, dichlorobenzene, trichlorobenzene, and tetrachlorobenzene) also have been shown to be readily biodegradable under aerobic conditions (Spain, 1996). Pentachlorobenzene and hexachlorobenzene are unlikely to be oxidized by microbial activity.

B.3.2.1.1 Aerobic Oxidation of Petroleum Hydrocarbons

Fuel hydrocarbons are rapidly biodegraded when they are utilized as the primary electron donor for microbial metabolism under aerobic conditions. Biodegradation of fuel hydrocarbons occurs naturally when sufficient oxygen (or other electron acceptors) and nutrients are available in the ground water. The rate of natural biodegradation is generally limited by the lack of oxygen or other electron acceptors rather than by the lack of nutrients such as nitrogen or phosphorus. The rate of natural aerobic biodegradation in unsaturated soil and shallow aquifers is largely dependent upon the rate at which oxygen enters the contaminated media. Biodegradation of fuel hydrocarbons is discussed by Wiedemeier *et al.* (1995a).

B.3.2.1.2 Aerobic Oxidation of Chlorinated Ethenes

In general, the highly chlorinated ethenes (e.g., PCE and TCE) are not likely to serve as electron donors or substrates for microbial degradation reactions. This is because the highly chlorinated compounds tend to be much more oxidized than many compounds present in a natural ground-water system.. Several microbes or microbial enrichments have been shown to be capable of TCE oxidation (Fogel *et al*., 1986; Nelson et al., 1986; Little et al., 1988); however, as noted by Vogel (1994), no strong evidence for the oxidation of highly chlorinated solvents has been derived from actual hazardous waste sites.

Using microcosms from two different sites with no prior history of exposure to DCE, Klier *et al*. (1998) show that all three isomers of DCE (i.e., 1,1-DCE, I-1,2-DCE, and *trans*-1,2-DCE) can be biodegraded in aerobic systems. In these experiments, it was observed that *cis*-1,2-DCE degraded more rapidly than the other isomers. Hartmans et al. (1985) and Hartmans and de Bont (1992) show that vinyl chloride can be used as a primary substrate under aerobic conditions, with vinyl chloride apparently being directly mineralized to carbon dioxide and water. This has also been reported by Davis and Carpenter (1990). Aerobic biodegradation is rapid relative to other mechanisms of vinyl chloride degradation, especially reductive dehalogenation.

B.3.2.1.3 Aerobic Oxidation of Chlorinated Ethanes

Of the chlorinated ethanes, only 1,2-dichloroethane has been shown to be aerobically mineralized/oxidized. Stucki *et al.* (1983) and Janssen *et al.* (1985) show that 1,2-DCA can be used as a primary substrate under aerobic conditions. In this case, the bacteria transform 1,2-DCA to chloroethanol, which is then mineralized to carbon dioxide. Evidence of oxidation of chloroethane is scant, however, it appears to rapidly degrade via abiotic mechanisms (hydrolysis) and is thus less likely to undergo biodegradation.

B.3.2.1.4 Aerobic Oxidation of Chlorobenzenes

Chlorobenzene and polychlorinated benzenes (up to and including tetrachlorobenzene) have been shown to be biodegradable under aerobic conditions. Several studies have shown that bacteria are able to utilize chlorobenzene (Reineke and Knackmuss, 1984), 1,4-DCB (Reineke and Knackmuss, 1984; Schraa *et al.*, 1986; Spain and Nishino, 1987), 1,3-DCB (de Bont *et al*., 1986), 1,2-DCB (Haigler *et al*., 1988), 1,2,4-TCB (van der Meer *et al*., 1987; Sander *et al*., 1991), and 1,2,4,5-TeCB (Sander *et al*., 1991) as primary growth substrates in aerobic systems. Nishino *et al*. (1994) note that aerobic bacteria able to grow on chlorobenzene have been detected at a variety of chlorobenzene-contaminated sites, but not at uncontaminated sites. Spain (1996) notes that this provides strong evidence that the bacteria are selected for their ability to derive carbon and energy from chlorobenzene degradation *in situ*.

The pathways for all of these reactions are similar, and are also similar to that of benzene (Chapelle, 1993; Spain, 1996). In general, the aerobic biodegradation involves hydroxylation of the chlorinated benzene to a chlorocatechol, followed by *ortho* cleavage of the benzene ring. This produces a muconic acid, which is dechlorinated, and the non-chlorinated intermediates are then metabolized. The only significant difference between this process and aerobic benzene degradation is the elimination of chlorine at some point in the pathway (Chapelle, 1993).

B.3.2.2 Anaerobic Biodegradation of Primary Substrates

Rapid depletion of dissolved oxygen caused by microbial respiration results in the establishment of anaerobic conditions in areas with high organic carbon concentrations. Certain requirements must be met in order for anaerobic (anoxic) bacteria to degrade organic compounds, including: absence of dissolved oxygen; availability of carbon sources (natural or anthropogenic), electron acceptors, and essential nutrients; and proper ranges of pH, temperature, salinity, and redox potential. When oxygen is absent, nitrate, manganese (IV), iron (III), sulfate, and carbon dioxide can serve as terminal electron acceptors during oxidation of organic carbon. While there is a large body of evidence for anaerobic mineralization (oxidation) of fuel hydrocarbons, there is very little evidence of such transformations involving chlorinated compounds.

B.3.2.2.1 Anaerobic Oxidation of Petroleum Hydrocarbons

Biodegradation of fuel hydrocarbons will occur under anaerobic conditions in most, if not all, ground-water environments via denitrification, manganese (IV) reduction, iron (III) reduction, sulfate reduction, and methanogenesis. Biodegradation of fuel hydrocarbons is discussed by Wiedemeier *et al.* (1995a), and many primary references are cited therein.

B.3.2.2.2 Anaerobic Oxidation of Chlorinated Ethenes

In general, due to the oxidized nature of polychlorinated ethenes, they are unlikely to undergo oxidation in groundwater systems. However, Bradley and Chapelle (1996) show that vinyl chloride (with only one chlorine substituent) can be directly oxidized to carbon dioxide and water via iron (III) reduction. Reduction of vinyl chloride concentrations in microcosms amended with iron (III)-EDTA closely matched the production of carbon dioxide. Slight mineralization was also noted in unamended microcosms. The rate of this reaction apparently depends on the bioavailability of the iron (III). At this time, it is not known if other workers have demonstrated other anaerobic mineralization reactions involving chlorinated ethenes.

B.3.2.2.3 Anaerobic Oxidation of Chlorinated Ethanes

During preparation of this protocol, no evidence of anaerobic oxidation of chlorinated ethanes was found; this does not necessarily indicate that such reactions have not been described. However, the lack of discussion of such transformations in surveys of chlorinated hydrocarbon biodegradation (e.g., Vogel et al., 1987; McCarty and Semprini, 1994; Vogel, 1994, Adriaens and Vogel, 1995; Spain, 1996) suggests that there has indeed been little, if any, work on this subject.

B.3.2.2.4 Anaerobic Oxidation of Chlorobenzenes

While aerobic mineralization of chlorobenzenes is similar to that of benzene, similar activity under anaerobic conditions has not been documented. As discussed above, there is little, if any, discussion of this topic in the literature.

B.3.3 BIODEGRADATION OF ORGANIC COMPOUNDS VIA USE AS AN ELECTRON ACCEPTOR (REDUCTIVE DECHLORINATION)

Bouwer *et al*. (1981) were the first to show that halogenated aliphatic hydrocarbons could be biologically transformed under anaerobic conditions in the subsurface environment. Since that time, numerous investigators have shown that chlorinated compounds can degrade via reductive dechlorination under anaerobic conditions. Anaerobically, biodegradation of chlorinated solvents most often proceeds through a process called reductive dechlorination. During this process, the halogenated hydrocarbon is used as an electron acceptor, not as a source of carbon, and a halogen atom is removed and replaced with a hydrogen atom. As an example, *Dehalobacter restrictus* was shown by Holliger *et al.,* (1993) to use tetrachloroethene as an electron acceptor during reductive dechlorination to produce *cis-1,2*-dichloroethene. Because chlorinated compounds are used as electron acceptors during reductive dechlorination, there must be an appropriate source of carbon for microbial growth in order for reductive dehalogenation to occur (Baek and Jaffe, 1989; Freedman and Gossett, 1989; Fathepure and Boyd, 1988; Bouwer, 1994). Potential carbon sources can include low molecular weight organic compounds (lactate, acetate, methanol, glucose, etc.), fuel hydrocarbons, byproducts of fuel degradation (e.g., volatile fatty acids), or naturally occurring organic matter.

In some situations, reductive dechlorination may be a cometabolic process, in that the reaction is incidental to normal metabolic functions and the organisms derive no benefit from the reaction. Such cometabolism typically results in slow, incomplete dechlorination (Gantzer and Wackett, 1991; Gossett and Zinder, 1996). More important, recent studies are discovering direct dechlorinators (typically isolated from contaminated subsurface environments or treatment systems) that use chlorinated ethenes as electron acceptors in reactions that provide growth and energy (e.g., Holliger *et al*., 1992; Holliger *et al*., 1993; Holliger and Schumacher, 1994; Neumann *et al*., 1994; Krumholz, 1995; Maymo-Gatell *et al*., 1995; Sharma and McCarty, 1996; Gerritse *et al*., 1996). This process has been termed both *halorespiration* and *dehalorespiration*.

Biotic transformations of chlorinated solvents under anaerobic conditions generally are reductions that involve either hydrogenolysis or dihaloelimination (McCarty and Semprini, 1994). Hydrogenolysis occurs when a chlorine atom is replaced with hydrogen. Dihaloelimination occurs when two adjacent chlorine atoms are removed and a double bond is formed between the respective carbon atoms. The most important process for the natural biodegradation of the more highly chlorinated solvents is reductive dechlorination (hydrogenolysis).

Higher ratios of chlorine to carbon represent higher oxidation levels; highly chlorinated compounds are more oxidized than lesser chlorinated compounds and thus are less susceptible to oxidation. Thus, highly chlorinated compounds such as PCE, TCE, TCA, or HCB are more likely to undergo reductive reactions than oxidative reactions. During these reductive reactions, electrons are transferred to the chlorinated compound, and a chlorine atom is replaced with a hydrogen atom. As an example, consider the reductive dechlorination of PCE to TCE and then TCE to DCE, and finally DCE to vinyl chloride. Because of the relatively low oxidation state of VC, this compound more commonly undergoes aerobic biodegradation as a primary substrate than reductive dechlorination.

Reductive dechlorination processes result in the formation of intermediates which are more reduced than the parent compound. These intermediates are often more susceptible to oxidative bacterial metabolism than to further reductive anaerobic processes. Actual mechanisms of reductive dehalogenation are still unclear, and in some cases may be a form of cometabolism (Gantzer and Wackett, 1991; Adriaens and Vogel, 1995; Wackett, 1995). In addition, other factors that will influ-

ence the process include the type of electron donor and the presence of competing electron acceptors (Adriaens and Vogel, 1995; Suflita and Townsend, 1995), temperature, and substrate availability.

Recent evidence suggests that dechlorination is dependent upon the supply of hydrogen (H_2), which acts as the electron donor in many such reactions (Gossett and Zinder, 1996; Smatlak *et al*., 1996). The hydrogen is produced as a result of the microbial degradation of a primary substrate (e.g., lactate, acetate, butyrate, ethanol, BTEX, or other such compounds). Bacteria that facilitate dechlorination compete with sulfate-reducers and methanogens for the H_2 produced in such a system. When degradation of the original substrate/electron donor rapidly yields high concentrations of H_2, the sulfate-reducers and methanogens appear to be favored over the dechlorinators. Conversely, when substrate degradation produces a steady supply of H_2 at low concentrations, the dechlorinators are favored (Gossett and Zinder, 1996; Smatlak *et al*., 1996). Complete dechlorination is thus apparently favored when a steady, low-concentration supply of H_2 is produced through microbial degradation of substrates such as proprionate or benzoate (and, by extension from benzoate, the BTEX compounds) (Gossett and Zinder, 1996). Therefore, the type of substrate/electron donor can also play a role in how thoroughly a natural system is able to dechlorinate solvents.

One or more of the following generally is observed at a site where reductive dechlorination of alkenes is ongoing:

1) Ethene is being produced (even low concentrations are indicative of biodegradation);
2) Methane is being produced;
3) Iron II is being produced;
4) Hydrogen concentrations are between 1-4 nM; and
5) Dissolved oxygen concentrations are low.

B.3.3.1 Reductive Dechlorination of Chlorinated Ethenes

PCE and TCE have been shown to undergo reductive dechlorination in a variety of anaerobic systems from different environments, with various electron donors/carbon sources (Table B.3.4) (Wilson, 1988; Sewell et al., 1991; Roberts et al., 1982). This is particularly true if the subsurface also contains other anthropogenic or native organic compounds that can serve as electron donors and whose utilization by subsurface bacteria will deplete any available oxygen. In general, reductive dechlorination of chlorinated ethenes occurs by sequential dechlorination from PCE to TCE to DCE to VC to ethene. Depending upon environmental conditions, this sequence may be interrupted, with other processes then acting upon the products. With sufficient quantities or appropriate types of electron donors (e.g., slow but steady H_2-production), the final end-product of anaerobic reductive dehalogenation can be ethene (Freedman and Gossett, 1989). Reductive dehalogenation of chlorinated solvent compounds is associated with the accumulation of daughter products and an increase in chloride.

Studies have shown that PCE and TCE can be anaerobically reduced to either 1,1-DCE, *cis*-1,2-DCE, or *trans*-1,2-DCE, all of which can be further transformed to vinyl chloride (Miller and Guengerich, 1982; Wilson and Wilson, 1985; Mayer *et al*., 1988; Nelson, *et al*., 1986; Henson *et al*., 1989; Tsien *et al*., 1989; Henry, 1991; McCarty, 1994; Wilson *et al*., 1994). During reductive dehalogenation, all three isomers of DCE can theoretically be produced; however, Bouwer (1994) reports that *cis-1,2*-DCE is a more common intermediate than *trans-1,2*-DCE and that *1,1*-DCE is the least prevalent intermediate of the three DCE isomers. Vinyl chloride produced from dehalogenation of DCE may be subsequently reduced to innocuous products such as ethane or carbon dioxide. The removal of vinyl chloride occurs more readily under aerobic conditions, such as those encountered at the edge of the plume. Vinyl chloride may also be used as a primary substrate by aerobic organisms, as previously discussed.

Table B.3.4 *Sources, Donors, Acceptors, and Products of Reductive Dechlorinating Laboratory Systems*

Reference	**Source**	**Donor**	**Acceptor-Product**
Bouwer & McCarty,1983	Digester	Organic Material	PCE-TCE
Vogel & McCarty, 1985	Bioreactor	Acetate	PCE-VC, CO_2
Kleopfer *et al*., 1985	Soil	Soybean Meal	TCE-DCE
Barrio-Lage *et al*., 1987	Swamp Muck	Organic Material	PCE-VC
	Soil	Methanol (?)	PCE-VC
Fathepure *et al*., 1987	Methanosarcina	Methanol	PCE-TCE
	DCB-1	3CB[a],Pyruvate,RF[b]	PCE-TCE
Baek & Jaffe, 1989	Digester	Formate	TCE-VC,CA[c]
		Methanol	TCE-VC,CA
Freedman & Gossett, 1989	Digester	Methanol	PCE-VC, Ethene
		Glucose	PCE-VC, Ethene
		H2	PCE-VC, Ethene
		Formate	PCE-VC, Ethene
		Acetate	PCE-VC, Ethene
Scholz-Muramatsu *et al*., 1990	Bioreactor	Benzoate	PCE-DCE
Gibson & Sewell, 1990	Aquifer	VFA[d]	PCE-DCE
Sewell & Gibson, 1990	Aquifer	Toluene	PCE-DCE
Sewell *et al*., 1991	Aquifer	VFA	PCE-DCE
	Landfill	VFA	PCE-VC
Lyon *et al*., 1995	Aquifer	Native Organic Matter	PCE-DCE

a 3-Chlorobenzoate
b Rumen Fluid
c Chloroethane
d Volatile Fatty Acid

B.3.3.2 Reductive Dechlorination of Chlorinated Ethanes

As with the ethenes, chlorinated ethanes will also undergo reductive dehalogenation in the subsurface via use as electron acceptors. Dechlorination of TCA has been described by Vogel and McCarty (1987) and Cox *et al*. (1995), but this pathway is complicated by the abiotic reactions that can affect TCA and its byproducts (Vogel, 1994).

B.3.3.3 Reductive Dechlorination of Chlorobenzenes

For the highly chlorinated benzenes (e.g., hexachlorobenzene and pentachlorobenzene, as well as tetrachlorobenzene, and trichlorobenzene), reductive dechlorination is the most likely biodegradation mechanism (Holliger *et al*., 1992; Ramanand *et al*., 1993; Suflita and Townsend, 1995). As discussed by Suflita and Townsend (1995), reductive dehalogenation of aromatic compounds has been observed in a variety of anaerobic habitats, including aquifer materials, marine and freshwater sediments, sewage sludges, and soil samples; however, isolation of specific microbes capable of these reactions has been difficult. As with the chlorinated ethenes and ethanes, the chlorobenzenes are most likely acting as electron acceptors as other sources of carbon and energy are being utilized by microbes or microbial consortia (Suflita and Townsend, 1995). Evidence has been presented suggesting that oxidation of hydrogen using halogenated aromatics as electron acceptors may yield more energy than if more commonly available electron acceptors were used (Dolfing and Harrison, 1992).

As discussed previously, the actual mechanisms of reductive dehalogenation are not well understood. Further, reductive dehalogenation of chlorinated benzenes has not been as well-documented as for other chlorinated solvents. However, reductive dechlorination of chlorobenzenes has been documented more frequently in the past several years (e.g., Bosma *et al*., 1988; Fathepure *et al*., 1988; Fathepure and Vogel, 1991; Holliger *et al*., 1992; Ramanand *et al*., 1993). As with other chlorinated solvents, the reductive dehalogenation of chlorobenzenes is affected by the degree of chlorination of the compound. The more chlorinated aromatic compounds are typically more amenable to this reaction (Suflita and Townsend, 1995; Adriaens and Vogel, 1995), but as they are dechlorinated, the daughter products will become more resistant to further dehalogenation reactions (Fathepure *et al*., 1988; Bosma *et al*., 1988; Holliger *et al*., 1992). The reductive dechlorination of chlorobenzenes is analogous to reactions involving chlorinated ethenes and ethanes in that such degradation will make them more amenable to aerobic biodegradation (Schraa, *et al*., 1986; Spain and Nishino, 1987; Ramanand *et al*., 1993).

B.3.4 BIODEGRADATION OF ORGANIC COMPOUNDS VIA COMETABOLISM

When a chlorinated solvent is biodegraded through cometabolism, it serves as neither an electron acceptor nor a primary substrate in a biologically mediated redox reaction. Instead, the degradation of the compound is catalyzed by an enzyme cofactor that is fortuitously produced by organisms for other purposes. The best-documented cometabolism reactions involve catabolic oxygenases that catalyze the initial step in oxidation of their respective primary or growth substrate (BTEX or other organic compounds). These oxygenases are typically nonspecific and, therefore, fortuitously initiate oxidation of a variety of compounds, including many of the CAHs (McCarty and Semprini, 1994). The organism receives no known benefit from the degradation of the chlorinated solvent; in some cases the cometabolic degradation of the solvent may, in fact, be harmful to the microorganism responsible for the production of the enzyme or cofactor (McCarty and Semprini, 1994). Chlorinated solvents are usually only partially transformed during cometabolic processes, with additional biotic or abiotic degradation generally required to complete the transformation (McCarty and Semprini, 1994).

Cometabolism is best documented for CAHs in aerobic environments; evidence of cometabolism of chlorobenzenes is scant, as is clear evidence of anaerobic cometabolism. In an

aerobic environment, many chlorinated organic compounds can only be degraded via cometabolism. It has been reported that under aerobic conditions chlorinated ethenes, with the exception of PCE, are susceptible to cometabolic degradation (Murray and Richardson, 1993; Vogel, 1994; McCarty and Semprini, 1994; Adriaens and Vogel, 1995). Vogel (1994) further elaborates that the oxidation rate increases as the degree of chlorination decreases. Aerobic cometabolism of ethenes may be characterized by a loss of contaminant mass, the presence of intermediate degradation products (e.g., chlorinated oxides, aldehydes, ethanols, and epoxides), and the presence of other products such as chloride, carbon dioxide, carbon monoxide, and a variety of organic acids (Miller and Guengerich, 1982; McCarty and Semprini, 1994).

The lack of clear evidence for anaerobic cometabolism does not necessarily imply that such transformations do not occur; in some cases, reductive dechlorination may be a result of cometabolism (e.g., Gantzer and Wackett, 1991), depending upon the relationship between the microbes, substrates, contaminants, and other electron acceptors. However, as with aerobic cometabolism, anaerobic cometabolism will be slow relative to dehalorespiration and might not be distinguishable at the field scale (Gossett and Zinder, 1996).

Several groups of aerobic bacteria currently are recognized as being capable of transforming TCE and other CAHs via cometabolism; these groups include:

- Methane Oxidizers (Methanotrophs) (Fogel *et al*., 1986; Little *et al*., 1988, Mayer *et al*., 1988; Oldenhuis *et al*., 1989; Tsien *et al*., 1989; Henry and Grbic-Galic, 1990; Alvarez-Cohen and McCarty, 1991a,b; Henry and Grbic-Galic, 1991a,b; Lanzarone and McCarty, 1990; Oldenhuis *et al.*, 1991);
- Propane Oxidizers (Wackett *et al*., 1989);
- Ethene Oxidizers (Henry, 1991);
- Toluene, Phenol, or Cresol Oxidizers (Nelson *et al*., 1986, 1987, 1988; Wackett and Gibson, 1988; Folsom *et al*., 1990; Harker and Kim, 1990);
- Ammonia Oxidizers (Arciero *et al*., 1989; Vannelli *et al*., 1990);
- Isoprene Oxidizers (Ewers *et al*., 1991); and
- Vinyl Chloride Oxidizers (Hartmans and de Bont, 1992).

These bacteria all have catabolic oxygenases that catalyze the initial step in oxidation of their respective primary or growth substrates and have the potential for initiating the oxidation of CAHs.

Cometabolism is not nearly as important a degradation mechanism for chlorinated solvents in the saturated zone as reductive dehalogenation. Due to the need for a substrate that may be present in limited concentrations, as well as the fortuitous nature of the reactions, rates of cometabolism are often slow enough that this process may not be detectable unless the system is stimulated with additional substrate mass. For a discussion of this topic, see McCarty and Semprini (1994) or Wackett (1995).

B.3.5 THERMODYNAMIC CONSIDERATIONS

Electron transfer results in oxidation of the electron donor and reduction of the electron acceptor and the production of usable energy. The energy produced by these reactions is quantified by the Gibbs free energy of the reaction (G_r) which is given by:

$$\Delta G_r^\circ = \sum \Delta G_{f,products}^\circ - \sum \Delta G_{f,reactants}^\circ \qquad \text{eq. B.3.1}$$

Where:

ΔG_r = Gibbs Free Energy of the Reaction at Standard State

$\Delta G_{f,products}$ = Gibbs Free Energy of Formation for Products at Standard State

$\Delta G_{f,reactants}$ = Gibbs Free Energy of Formation for the Reactants at Standard State

The G_r defines the maximum useful energy change for a chemical reaction at a constant temperature and pressure. Table B.3.5 presents select electron acceptor and electron donor half-cell reactions and the calculated G_r values. Table B.3.6 gives the Gibbs free energy of formation (G_f) for species used in these half-cell reactions. Table B.3.7 presents coupled oxidation-reduction reactions. In general, those reactions that yield the most energy tend to take precedence over less energy-yielding reactions. However, the calculated energy yield of processes involving anthropogenic organic compounds may not be reflected in the true energy yield of the metabolic process. Figure B.3.4 illustrates the expected sequence of microbially mediated redox reactions based on G_r. There is sufficient energy in the reaction of fuel hydrocarbons with chlorinated solvents to allow their use by microorganisms as physiological electron acceptors.

Table B.3.5 *Electron Donor and Electron Acceptor Half-Cell Reactions*

HALF-CELL REACTIONS	$\Delta G°_r$ (kcal/ equiv)*	$\Delta G°_r$ (kJ/ equiv)*	E° (V)	Eh (V)	pe	Conditions for Eh and pe §
ELECTRON-ACCEPTOR (REDUCTION) HALF CELL REACTIONS						
$5e^- + 6H^+ + NO_3^- \Rightarrow 0.5N_2 + 3H_2O$ *Denitrification*	-28.7	-120.	+1.24	+0.708	+12.0	pH = 7 $\Sigma[N]=10^{-3}$
$4e^- + 4H^+ + O_2 \Rightarrow 2H_2O$ *Aerobic Respiration*	-28.3	-119.	+1.23	+0.805	+13.6	pH = 7 $P_{O_2}=0.21$ atm
$2e^- + 4H^+ + \underline{MnO_2} \Rightarrow Mn^{2+} + 2H_2O$ *Pyrolusite Dissolution/Reduction*	-28.3	-119	+1.23	+1.169	+19.8	pH = 7 $\Sigma[Mn]=10^{-5}$
$CO_2 + e^- + H^+ + \underline{MnOOH} \Rightarrow MnCO_3 + H_2O$ *Manganite Carbonation/Reduction*	-23.1	-96.8	+1.00	+0.408	+6.90	pH = 8 $P_{CO_2}=10^{-2}$
$e^- + H^+ + MnO_2 \Rightarrow \underline{MnOOH}$ *Pyrolusite Hydrolysis/Reduction*	-22.1	-92.5	+0.959	+0.545	+9.21	pH = 7
$e^- + 3H^+ + \underline{Fe(OH)_{3,amph.}} \Rightarrow Fe^{2+} + 3H_2O$ *Amorphous "Goethite" Dissolution/Reduction*	-21.5	-89.9	+0.932	+0.163	+2.75	pH = 6 $\Sigma[Fe]=10^{-5}$
$8e^- + 10H^+ + NO_3^- \Rightarrow NH_4^+ + 3H_2O$ *Nitrate Reduction*	-20.3	-84.9	+0.879	+0.362	+6.12	pH = 7
$2e^- + 2H^+ + NO_3^- \Rightarrow NO_2^- + H_2O$ *Nitrate Reduction*	-18.9	-78.9	+0.819	+0.404	+6.82	pH = 7
$e^- + 3H^+ + \underline{FeOOH} \Rightarrow Fe^{2+} + 2H_2O$ *"Ferric oxyhydroxide" Dissolution/Reduction*	-15.0	-62.9	+0.652	-0.118	-1.99	pH = 6 Σ [Fe]=10^{-5}
$e^- + 3H^+ + \underline{Fe(OH)_{3,xline.}} \Rightarrow Fe^{2+} + 3H_2O$ *Crystallized "Goethite" Dissolution/Reduction*	-11.8	-49.2	+0.510	-0.259	-4.38	pH = 6 Σ [Fe]=10^{-5}
$e^- + H^+ + CO_{2,g} + \underline{Fe(OH)_{3,amph.}} \Rightarrow \underline{FeCO_3} + 2H_2O$ *Amorphous "Goethite" Carbonation/Reduction*	-11.0	-46.2	+0.479	-0.113	-1.90	pH = 8 $P_{CO_2}=10^{-2}$ atm
$8e^- + 9H^+ + SO_4^{2-} \Rightarrow HS^- + 4H_2O$ *Sulfate Reduction*	-5.74	-24.0	+0.249	-0.278	-4.70	pH = 8
$8e^- + 10H^+ + SO_4^{2-} \Rightarrow H_2S^o + 4H_2O$ *Sulfate Reduction*	-6.93	-28.9	+0.301	-0.143	-2.42	pH = 6
$8e^- + 8H^+ + CO_{2,g} \Rightarrow CH_{4,g} + 2H_2O$ *Methanogenesis*	-3.91	-16.4	+0.169	-0.259	-4.39	pH = 7 $P_{CO_2}=10^{-2}$ $P_{CH_4}=10^{0}$
$C_2Cl_4 + H^+ + 2e^- \Rightarrow C_2HCl_3 + Cl^-$ *PCE Reductive Dechlorination*	-14.79	-61.8	+0.641	+0.552	+9.33	pH = 7 $[Cl^-]=10^{-4}$
$C_2HCl_3 + H^+ + 2e^- \Rightarrow C_2H_2Cl_2 + Cl^-$ *TCE Reductive Dechlorination*	-14.50	-60.6	+0.628	+0.539	+9.12	pH = 7 $[Cl^-]=10^{-4}$
$C_2H_2Cl_2 + H^+ + 2e^- \Rightarrow C_2H_3Cl + Cl^-$ *c-DCE Reductive Dechlorination*	-12.12	-50.7	+0.525	+0.436	+7.38	pH = 7 $[Cl^-]=10^{-4}$
$C_2H_3Cl + H^+ + 2e^- \Rightarrow C_2H_4 + Cl^-$ *VC Reductive Dechlorination*	-13.75	-57.5	+0.596	+0.507	+8.57	pH = 7 $[Cl^-]=10^{-4}$
$C_2H_2Cl_4 + H^+ + 2e^- \Rightarrow C_2H_3Cl_3 + Cl^-$ *PCA Reductive Dechlorination*	-13.59	-56.8	+0.589	+0.500	+8.45	pH = 7 $[Cl^-]=10^{-4}$
$C_2H_3Cl_3 + H^+ + 2e^- \Rightarrow C_2H_4Cl_2 + Cl^-$ *TCA Reductive Dechlorination*	-15.26	-63.8	+0.661	+0.572	+9.67	pH = 7 $[Cl^-]=10^{-4}$
$C_2H_4Cl_2 + H^+ + 2e^- \Rightarrow C_2H_5Cl + Cl^-$ *DCA Reductive Dechlorination*	-14.08	-58.9	+0.610	+0.521	+8.81	pH = 7 $[Cl^-]=10^{-4}$
$C_6Cl_6 + H^+ + 2e^- \Rightarrow C_6HCl_5 + Cl^-$ *Hexachlorobenzene Reductive Dechlorination*	-14.36	-60.0	+0.622	+0.533	+9.01	pH = 7 $[Cl^-]=10^{-4}$
$C_6HCl_5 + H^+ + 2e^- \Rightarrow C_6H_2Cl_4 + Cl^-$ *Pentachlorobenzene Reductive Dechlorination*	-14.64	-61.2	+0.634	+0.545	+9.22	pH = 7 $[Cl^-]=10^{-4}$
$C_6H_2Cl_4 + H^+ + 2e^- \Rightarrow C_6H_3Cl_3 + Cl^-$ *Tetrachlorobenzene Reductive Dechlorination*	-13.66	-57.1	+0.592	+0.503	+8.50	pH = 7 $[Cl^-]=10^{-4}$
$C_6H_3Cl_3 + H^+ + 2e^- \Rightarrow C_6H_4Cl_2 + Cl^-$ *Trichlorobenzene Reductive Dechlorination*	-13.20	-55.2	+0.572	+0.483	+8.17	pH = 7 $[Cl^-]=10^{-4}$

Table B.3.5 *Continued.*

HALF-CELL REACTIONS	$\Delta G°_r$ (kcal/equiv)*	$\Delta G°_r$ (kJ/equiv)*	E° (V)	Eh (V)	pe	Conditions for Eh and pe §
ELECTRON-DONOR (OXIDATION) HALF CELL REACTIONS						
$12H_2O + C_6H_6 \Rightarrow 6CO_2 + 30H^+ + 30e^-$ *Benzene Oxidation*	+2.83	+11.8	-0.122	+0.316	+5.34	pH = 7 $P_{CO_2}=10^{-2}$
$14H_2O + C_6H_5CH_3 \Rightarrow 7CO_2 + 36H^+ + 36e^-$ *Toluene Oxidation*	+2.96	+12.4	-0.128	+0.309	+5.22	pH = 7 $P_{CO_2}=10^{-2}$
$16H_2O + C_6H_5C_2H_5 \Rightarrow 8CO_2 + 42H^+ + 42e^-$ *Ethylbenzene Oxidation*	+2.96	+12.4	-0.128	+0.309	+5.21	pH = 7 $P_{CO_2}=10^{-2}$
$16H_2O + C_6H_4(CH_3)_2 \Rightarrow 8CO_2 + 42H^+ + 42e^-$ *m-Xylene Oxidation*	+3.03	+12.7	-0.132	+0.303	+5.12	pH = 7 $P_{CO_2}=10^{-2}$
$20H_2O + C_{10}H_8 \Rightarrow 10CO_2 + 48H^+ + 48e^-$ *Naphthalene Oxidation*	+2.98	+12.5	-0.130[a]	+0.309	+5.22	pH = 7 $P_{CO_2}=10^{-2}$
$18H_2O + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48H^+ + 48e^-$ *1,3,5-Trimethylbenzene Oxidation*	+3.07	+12.8	-0.133[a]	+0.303	+5.12	pH = 7 $P_{CO_2}=10^{-2}$
$18H_2O + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48H^+ + 48e^-$ *1,2,4-Trimethylbenzene Oxidation*	+3.07	+12.9	-0.134[a]	+0.302	+5.11	pH = 7 $P_{CO_2}=10^{-2}$
$4H_2O + C_2H_2Cl_2 \Rightarrow 2CO_2 + 10H^+ + 8e^- + 2C1^-$ *DCE Oxidation*	-3.88	-16.2	+0.168	-0.131	-2.21	pH = 7 $P_{CO_2}=10^{-2}$
$4H_2O + C_2H_3Cl \Rightarrow 2CO_2 + 11H^+ + 10e^- + C1^-$ *Vinyl Chloride Oxidation*	-0.55	-2.31	+0.024[a]	-0.006	-0.10	pH = 7 $P_{CO_2}=10^{-2}$
$12H_2O + C_6H_2Cl_4 \Rightarrow 6CO_2 + 26H^+ + 22e^- + 4Cl^-$ *Tetrachlorobenzene Oxidation*	-0.64	-2.68	+0.028	+0. 016	+0.27	pH = 7 $P_{CO_2}=10^{-2}$
$12H_2O + C_6H_3Cl_3 \Rightarrow 6CO_2 + 27H^+ + 24e^- + 3Cl^-$ *Trichlorobenzene Oxidation*	+0.42	+1.77	-0.018	-0.030	-0.50	pH = 7 $P_{CO_2}=10^{-2}$
$12H_2O + C_6H_4Cl_2 \Rightarrow 6CO_2 + 28H^+ + 26e^- + 2Cl^-$ *Dichlorobenzene Oxidation*	+1.40	+5.84	-0.060	-0.071	-1.21	pH = 7 $P_{CO_2}=10^{-2}$
$12H_2O + C_6H_5Cl \Rightarrow 6CO_2 + 29H^+ + 28e^- + Cl^-$ *Chlorobenzene Oxidation*	+2.22	+9.26	-0.096[a]	-0.107	-1.80	pH = 7 $P_{CO_2}=10^{-2}$

NOTES:

* = $\Delta G°_r$ for half-cell reaction as shown divided by the number of electrons involved in reaction.

§ = Conditions assumed for the calculation of Eh and pe (pe = Eh/0.05916). Where two dissolved species are involved, other than those mentioned in this column, their activities are taken as equal. Note, this does not affect the free energy values listed.

[a] = E^o calculated using the following equation; $E^o = \Delta G°_r$ (J/nF) * 1.0365×10^{-5} (VF/J) from Stumm and Morgan, 1981.

Table B.3.6 *Gibbs Free Energy of Formation for Species used in Half-Cell Reactions and Coupled Oxidation-Reduction Reactions*

Species	State	$\Delta G^{o}_{f,298.15}$ (kcal/mole)	Source
e^-	i	0	std
H^+	i	0	std
O_2	g	0	std
H_2O	l	-56.687	Dean (1972)
Carbon Species			
CO_2	g	-94.26	Dean (1972)
CH_2O, formaldehyde	aq	-31.02	Dean (1972)
C_6H_6, benzene	l	+29.72	Dean (1972)
CH_4, methane	g	-12.15	Dean (1972)
$C_6H_5CH_3$, toluene	l	+27.19	Dean (1972)
$C_6H_5C_2H_5$, ethylbenzene	l	+28.61	Dean (1972)
$C_6H_4(CH_3)_2$, o-xylene	l	+26.37	Dean (1972)
$C_6H_4(CH_3)_2$, m-xylene	l	+25.73	Dean (1972)
$C_6H_4(CH_3)_2$, p-xylene	l	+26.31	Dean (1972)
C_2Cl_4, PCE	l	+1.1	CRC Handbook (1996)
C_2HCl_3, TCE	l	+2.9	CRC Handbook (1996)
$C_2H_2Cl_2$ 1,1-dichloroethene	l	+5.85	Dean (1972)
$C_2H_2Cl_2$ cis-1,2-dichloroethene	l	5.27	CRC Handbook (1996)
$C_2H_2Cl_2$ trans-1,2-dichloroethene	l	+6.52	CRC Handbook (1996)
C_2H_4 Ethene	g aq, m=1	+16.28 +19.43	CRC Handbook (1996)
C_2H_6 Ethane	g aq, m=1	-7.68 -4.09	CRC Handbook (1996)
HCl hydrochloric acid	aq, m=1	-31.372	CRC Handbook (1996)a
$C_2H_2Cl_4$, 1,1,2,2-PCA	l	-22.73	Dean (1972)
$C_2H_3Cl_3$, 1,1,2-TCA	g	-18.54	Dean (1972)
$C_2H_4Cl_2$, 1,2-DCA	g	-17.68	Dean (1972)
$C_2H_5Cl_1$, Chloroethane	g	-14.47	Dean (1972)
$C_{10}H_8$, naphthalene	l	+48.05	Dean (1972)
$C_6H_3(CH_3)_3$, 1,3,5-TMB	1	+24.83	Dean (1972)
$C_6H_3(CH_3)_3$, 1,2,4-TMB	1	+24.46	Dean (1972)
C_2H_3Cl, Vinyl chloride	g	+12.4	Dean (1972)
C_6Cl_6, Hexachlorobenzene	l	+0.502	Dolfing and Harrison (1992)
$C_6H_1Cl_5$, Pentachlorobenzene	l	+3.16	Dolfing and Harrison (1992)
$C_6H_2Cl_4$, 1,2,4,5-Tetrachlorobenzene	l	+5.26	Dolfing and Harrison (1992)
$C_6H_3Cl_3$, 1,2,4-Trichlorobenzene	l	+9.31	Dolfing and Harrison (1992)
$C_6H_4Cl_2$, 1,4-Dichlorobenzene	l	+14.28	Dolfing and Harrison (1992)
C_6H_5Cl, chlorobenzene	1	+21.32	Dean (1972)
$C_{14}H_{10}$, phenanthrene	l	+64.12	Dean (1972)

Table B.3.6 *Continued.*

Species	State	$\Delta G^{o}_{f,298.15}$ (kcal/mole)	Source
Nitrogen Species			
NO_3^-	I	-26.61	Dean (1972)
N_2	g	0	std
NO_2^-	I	-7.7	Dean (1972)
NH_4^+	aq	-18.97	Dean (1972)
Sulfur Species			
SO_4^{2-}	i	-177.97	Dean (1972)
H_2S	aq	-6.66	Dean (1972)
H_2S	g	-7.9	Dean (1972)
HS^-	i	+2.88	Dean (1972)
Iron Species			
Fe^{2+}	i	-18.85	Dean (1972)
Fe^{3+}	i	-1.1	Dean (1972)
Fe_2O_3, hematite	c	-177.4	Dean (1972)
FeOOH, ferric oxyhydroxide	c	-117.2	Naumov *et al.* (1974)
$Fe(OH)_3$, goethite	a	-167.416	Langmuir and Whittemore (1971)
$Fe(OH)_3$, goethite	c	-177.148	Langmuir and Whittemore (1971)
$FeCO_3$, siderite	c	-159.35	Dean (1972)
Manganese Species			
Mn^{2+}	i	-54.5	Dean (1972)
MnO_2, pyrolusite	c	-111.18	Stumm and Morgan (1981)
MnOOH, manganite	c	-133.29	Stumm and Morgan (1981)
$MnCO_3$, rhodochrosite	p	-194	Dean (1972)
Chloride Species			
Cl^-	aq	-31.37	Dean (1972)

NOTES:

c = crystallized solid l = liquid g = gaseous aq = undissociated aqueous species
a = amorphous solid (may be partially crystallized - dependent on methods of preparation)
p = freshly precipitated solid
i = dissociated, aqueous ionic species (concentration = 1 m)
std = accepted by convention
Wherever possible multiple sources were consulted to eliminate the possibility of typographical error.

Table B.3.7 *Coupled Oxidation-Reduction Reactions*

Coupled Benzene Oxidation Reactions	$\Delta G°_r$ (kcal/mole)	$\Delta G°_r$ (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$7.5O_2 + C_6H_6 \Rightarrow 6CO_{2,g} + 3H_2O$ *Benzene oxidation /aerobic respiration*	-765.34	-3202	3.07:1	0.326:1
$6NO_3^- + 6H^+ + C_6H_6 \Rightarrow 6CO_{2,g} + 6H_2O + 3N_{2,g}$ *Benzene oxidation / denitrification*	-775.75	-3245	4.77:1	0.210:1
$30H^+ + 15\underline{MnO_2} + C_6H_6 \Rightarrow 6CO_{2,g} + 15Mn^{2+} + 18H_2O$ *Benzene oxidation / manganese reduction*	-765.45	-3202	10.56:1	0.095:1
$3.75\ NO_3^- + C_6H_6 + 7.5\ H^+ + 0.75\ H_2O \Rightarrow 6\ CO_2 + 3.75\ NH_4^+$ *Benzene oxidation / nitrate reduction*	-524.1	-2193	2.98:1	0.336:1
$60H^+ + 30\underline{Fe(OH)_{3,a}} + C_6H_6 \Rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O$ *Benzene oxidation / iron reduction*	-560.10	-2343	21.5:1	0.047:1
$7.5H^+ + 3.75SO_4^{2-} + C_6H_6 \Rightarrow 6\,CO_{2,g} + 3.75H_2S^o + 3H_2O$ *Benzene oxidation / sulfate reduction*	-122.93	-514.3	4.61:1	0.22:1
$4.5H_2O + C_6H_6 \Rightarrow 2.25CO_{2,g} + 3.75CH_4$ *Benzene oxidation / methanogenesis*	-32.40	-135.6	0.77:1	1.30:1
$15\ C_2H_2Cl_4 + C_6H_6 + 12\ H_2O \Rightarrow 6\ CO_2 + 15\ C_2H_3Cl_3 + 15\ H^+ + 15\ Cl^-$ *Benzene oxidation / PCA reduction*	-322.7	-1349	32.2:1	0.03:1
$15\ C_2H_3Cl_3 + C_6H_6 + 12\ H_2O\ 6 \Rightarrow CO_2 + 15\ C_2H_4Cl_2 + 15\ H^+ + 15\ Cl^-$ *Benzene oxidation / TCA reduction*	-372.65	-1558	25.6:1	0.04:1
$15\ C_2H_4Cl_2 + C_6H_6 + 12\ H_2O \Rightarrow 6\ CO_2 + 15\ C_2H_5Cl + 15\ H^+ + 15\ Cl^-$ *Benzene oxidation / DCA reduction*	-337.40	-1410	19.0:1	0.05:1
$15C_2Cl_4 + 12H_2O + C_6H_6 \Rightarrow 15C_2HCl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ Tetrachloroethylene reductive dehalogenation*	-358.55	-1499	31.8:1	0.03:1
$15C_2HCl_3 + 12H_2O + C_6H_6 \Rightarrow 15C_2H_2Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ Trichloroethylene reductive dehalogenation*	-331.25	-1385	25.2:1	0.04:1
$15C_2H_2Cl_2 + 12H_2O + C_6H_6 \Rightarrow 15C_2H_3Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-297.35	-1243	18.6:1	0.05:1
$15C_2H_3Cl + 12H_2O + C_6H_6 \Rightarrow 15C_2H_4 + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ Vinyl chloride reductive dehalogenation*	-327.35	-1368	12.0:1	0.08:1
$15C_6Cl_6 + 12H_2O + C_6H_6 \Rightarrow 15C_6H_1Cl_5 + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ Hexachlorobenzene reductive dehalogenation*	-345.68	-1445	54.7:1	0.02:1
$15C_6H_1Cl_5 + 12H_2O + C_6H_6 \Rightarrow 15C_6H_2Cl_4 + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ Pentachlorobenzene reductive dehalogenation*	-354.05	-1480	48.1:1	0.02:1
$15C_6H_2Cl_4 + 12H_2O + C_6H_6 \Rightarrow 15C_6H_3Cl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ Tetrachlorobenzene reductive dehalogenation*	-324.80	-1358	41.5:1	0.02:1
$15C_6H_3Cl_3 + 12H_2O + C_6H_6 \Rightarrow 15C_6H_4Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Benzene oxidation/ Trichlorobenzene reductive dehalogenation*	-311.0	-1300	34.8:1	0.03:1

Table B.3.7 *Continued.*

Coupled Toluene Oxidation Reactions	$\Delta G°_r$ (kcal/ mole)	$\Delta G°_r$ (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$9O_2 + C_6H_5CH_3 \Rightarrow 7CO_{2g} + 4H_2O$ *Toluene oxidation /aerobic respiration*	-913.76	-3823	3.13:1	0.32:1
$7.2NO_3 + 7.2H^+ + C_6H_5CH_3 \Rightarrow 7CO_{2g} + 7.6H_2O + 3.6N_{2g}$ *Toluene oxidation / denitrification*	-926.31	-3875	4.85:1	0.21:1
$36H^+ + 18\underline{MnO_2} + C_6H_5CH_3 \Rightarrow 7CO_{2g} + 18Mn^{2+} + 22H_2O$ *Toluene oxidation / manganese reduction*	-913.89	-3824	10.74:1	0.09:1
$72H^+ + 36\underline{Fe(OH)_{3a}} + C_6H_5CH_3 \Rightarrow 7CO_2 + 36Fe^{2+} + 94H_2O$ *Toluene oxidation / iron reduction*	-667.21	-2792	21.86:1	0.05:1
$9H^+ + 4.5SO_4^{2-} + C_6H_5CH_3 \Rightarrow 7CO_{2g} + 4.5H_2S^o + 4H_2O$ *Toluene oxidation / sulfate reduction*	-142.86	-597.7	4.7:1	0.21:1
$5H_2O + C_6H_5CH_3 \Rightarrow 2.5CO_{2g} + 4.5CH_4$ *Toluene oxidation / methanogenesis*	-34.08	-142.6	0.78:1	1.28:1
$18\ C_2H_2Cl_4 + C_6H_5CH_3 + 14\ H_2O \Rightarrow 7\ CO_2 + 18\ C_2H_3Cl_3 + 18H^+ + 18Cl^-$ *Toluene oxidation / PCA reduction*	-382.6	-1599	32.8:1	0.03:1
$18\ C_2H_3Cl_3 + C_6H_5CH_3 + 14\ H_2O \Rightarrow 7\ CO_2 + 18\ C_2H_4Cl_2 + 18H^+ + 18Cl^-$ *Toluene oxidation / TCA reduction*	-442.5	-1850	26.1:1	0.04:1
$18\ C_2H_4Cl_2 + C_6H_5CH_3 + 14\ H_2O \Rightarrow 7\ CO_2 + 18\ C_2H_5Cl + 18\ H^+ + 18\ Cl^-$ *Toluene oxidation / DCA reduction*	-400.2	-1673	19.3:1	0.05:1
$18C_2Cl_4 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2HCl_3 + 7CO_2 + 18H^+ + 18Cl^-$ *Toluene oxidation/ Tetrachloroethylene reductive dehalogenation*	-425.6	-1779	32.4:1	0.03:1
$18C_2HCl_3 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2H_2Cl_2 + 7CO_2 + 18H^+ + 18Cl^-$ *Toluene oxidation/ Trichloroethylene reductive dehalogenation*	-404.9	-1693	25.7:1	0.04:1
$18C_2H_2Cl_2 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2H_3Cl + 7CO_2 + 18H^+ + 18Cl^-$ *Toluene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-340.1	-1422	18.9:1	0.05:1
$18C_2H_3Cl + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_2H_4 + 7CO_2 + 18H^+ + 18Cl^-$ *Toluene oxidation/ Vinyl chloride reductive dehalogenation*	-331.5	-1386	12.2:1	0.08:1
$18C_6Cl_6 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_6H_1Cl_5 + 7CO_2 + 18H^+ + 18Cl$ *Toluene oxidation/ Hexachlorobenzene reductive dehalogenation*	-410.3	-1715	55.6:1	0.02:1
$18C_6H_1Cl_5 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_6H_2Cl_4 + 7CO_2 + 18H^+ + 18Cl$ *Toluene oxidation/ Pentachlorobenzene reductive dehalogenation*	-420.3	-1757	48.9:1	0.02:1
$18C_6H_2Cl_4 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_6H_3Cl_3 + 7CO_2 + 18H^+ + 18Cl$ *Toluene oxidation/ Tetrachlorobenzene reductive dehalogenation*	-385.2	-1610	42.2:1	0.02:1
$18C_6H_3Cl_3 + 14H_2O + C_6H_5CH_3 \Rightarrow 18C_6H_4Cl_2 + 7CO_2 + 18H^+ + 18Cl$ *Toluene oxidation/ Trichlorobenzene reductive dehalogenation*	-368.6	-1541	35.4:1	0.03:1

Table B.3.7 *Continued.*

Coupled Ethylbenzene Oxidation reactions	$\Delta G°_r$ kcal/ mole	$\Delta G°_r$ kJ/ mole	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$10.5O_2 + C_6H_5C_2H_5 \Rightarrow 8CO_{2,g} + 5H_2O$ *Ethylbenzene oxidation /aerobic respiration*	-1066.13	-4461	3.17:1	0.32:1
$8.4NO_3 + 8.4H^+ + C_6H_5C_2H_5 \Rightarrow 8CO_{2,g} + 9.2H_2O + 4.2N_{2,g}$ *Ethylbenzene oxidation / denitrification*	-1080.76	-4522	4.92:1	0.20:1
$46H^+ + 22\underline{MnO_2} + C_6H_5C_2H_5 \Rightarrow 8CO_{2,g} + 22Mn^{2+} + 28H_2O$ *Ethylbenzene oxidation / manganese reduction*	-1066.27	-4461	11.39:1	0.09:1
$84H^+ + 42\underline{Fe(OH)_{3,a}} + C_6H_5C_2H_5 \Rightarrow 8CO_2 + 42Fe^{2+} + 110H_2O$ *Ethylbenzene oxidation / iron reduction*	-778.48	-3257	22.0:1	0.05:1
$10.5H^+ + 5.25SO_4^{2-} + C_6H_5C_2H_5 \Rightarrow 8CO_{2,g} + 5.25H_2S^o + 5H_2$ *Ethylbenzene oxidation / sulfate reduction*	-166.75	-697.7	4.75:1	0.21:1
$5.5H_2O + C_6H_5C_2H_5 \Rightarrow 2.75CO_{2,g} + 5.25CH_4$ *Ethylbenzene oxidation / methanogenesis*	-39.83	-166.7	0.79:1	1.27:1
$21C_2H_2Cl_4 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_3Cl_3 + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ PCA reductive dehalogenation*	-446.43	-1866	32.8:1	0.03:1
$21C_2H_3Cl_3 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_4Cl_2 + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ TCA reductive dehalogenation*	-516.36	-2158	26.1:1	0.04:1
$21C_2H_4Cl_2 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_5Cl + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ DCA reductive dehalogenation*	-467.01	-1952	19.4:1	0.05:1
$21C_2Cl_4 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2HCl_3 + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ Tetrachloroethylene reductive dehalogenation*	-496.67	-2078	32.8:1	0.03:1
$21C_2HCl_3 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_2Cl_2 + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ Trichloroethylene reductive dehalogenation*	-484.70	-2028	26.0:1	0.04:1
$21C_2H_2Cl_2 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_3Cl + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-384.74	-1610	19.2:1	0.05:1
$21C_2H_3Cl + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_2H_4 + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ Vinyl chloride reductive dehalogenation*	-368.79	-1617	12.3:1	0.08:1
$21C_6Cl_6 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_6H_1Cl_5 + 8CO_2 + 21H^+ + 21Cl$ *Ethylbenzene oxidation/ Hexachlorobenzene reductive dehalogenation*	-478.7	-2001	55.6:1	0.02:1
$21C_6H_1Cl_5 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_6H_2Cl_4 + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ Pentachlorobenzene reductive dehalogenation*	-490.4	-2050	48.9:1	0.02:1
$21C_6H_2Cl_4 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_6H_3Cl_3 + 8CO_2 + 21H^+ + 21Cl$ *Ethylbenzene oxidation/ Tetrachlorobenzene reductive dehalogenation*	-449.4	-1878	42.2:1	0.02:1
$21C_6H_3Cl_3 + 16H_2O + C_6H_5C_2H_5 \Rightarrow 21C_6H_4Cl_2 + 8CO_2 + 21H^+ + 21Cl^-$ *Ethylbenzene oxidation/ Trichlorobenzene reductive dehalogenation*	-430.1	-1794	35.5:1	0.03:1

Table B.3.7 *Continued.*

Coupled m-Xylene Oxidation Reactions	$\Delta G°_r$ (kcal/ mole)	$\Delta G°_r$ (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$10.5\ O_2 + C_6H_4(CH_3)_2 \Rightarrow 8CO_2 + 5\ H_2O$ *m-Xylene oxidation / aerobic respiration*	-1063.25	-4448	3.17:1	0.32:1
$8.4\ H^+ + 8.4NO^-_3 + C_6H_4(CH_3)_2 \Rightarrow 8CO_2 + 4.2\ N_2 + 9.2\ H_2O$ *m-Xylene oxidation / denitrification*	-1077.81	-4509	4.92:1	0.20:1
$46\ H^+ + 22MnO_2 + C_6H_4(CH_3)_2 \Rightarrow 8CO_2 + 22\ Mn^{2+} + 28\ H_2O$ *m-Xylene oxidation / manganese reduction*	-1063.39	-4449	11.39:1	0.09:1
$84\ H^+ + 42Fe(OH)_{3,a} + C_6H_4(CH_3)_2 \Rightarrow 8CO_2 + 42\ Fe^{2+} + 110\ H_2O$ *m-Xylene oxidation / iron reduction*	-775.61	-3245	22:1	0.05:1
$10.5H^+ + 5.25SO_4^{2-} + C_6H_4(CH_3)_2 \Rightarrow 8CO_2 + 5.25\ H_2S^o + 5\ H_2O$ *m-Xylene oxidation / sulfate reduction*	-163.87	-685.6	4.75:1	0.21:1
$5.5H_2O + C_6H_4(CH_3)_2 \Rightarrow 2.75CO_2 + 5.25CH_4$ *m-Xylene oxidation / methanogenesis*	-36.95	-154.6	0.79:1 [a/]	1.27:1
$21C_2H_2Cl_4 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_3Cl_3 + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ PCA reductive dehalogenation*	-445.70	-1863	32.7:1	0.03:1
$21C_2\ H_3Cl_3 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_4Cl_2 + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ TCA reductive dehalogenation*	-513.48	-2146	26.0:1	0.04:1
$21C_2H_4Cl_2 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_5Cl + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ DCA reductive dehalogenation*	-464.13	-1940	19.3:	0.05:1
$21C_2Cl_4 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2HCl_3 + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ Tetrachloroethylene reductive dehalogenation*	-493.79	-2066	32.8:1	0.03:1
$21C_2HCl_3 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_2Cl_2 + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ Trichloroethylene reductive dehalogenation*	-469.59	-1963	26.0:1	0.04:1
$21C_2H_2Cl_2 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_3Cl + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ cis-Dichloroethylene reductive dehalogenation*	-393.99	-1647	19.2:1	0.05:1
$21C_2H_3Cl + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_2H_4 + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ Vinyl chloride reductive dehalogenation*	-383.91	-1605	12.3:1	0.08:1
$21C_6Cl_6 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_6H_1Cl_5 + 8CO_2 + 21H^+ + 21Cl$ *m-Xylene oxidation/ Hexachlorobenzene reductive dehalogenation*	-475.9	-1989	55.6:1	0.02:1
$21C_6H_1Cl_5 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_6H_2Cl_4 + 8CO_2 + 21H^+ + 21Cl$ *m-Xylene oxidation/ Pentachlorobenzene reductive dehalogenation*	-487.5	-2038	48.9:1	0.02:1
$21C_6H_2Cl_4 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_6H_3Cl_3 + 8CO_2 + 21H^+ + 21Cl$ *m-Xylene oxidation/ Tetrachlorobenzene reductive dehalogenation*	-446.6	-1867	42.2:1	0.02:1
$21C_6H_3Cl_3 + 16H_2O + C_6H_4(CH_3)_2 \Rightarrow 21C_6H_4Cl_2 + 8CO_2 + 21H^+ + 21Cl^-$ *m-Xylene oxidation/ Trichlorobenzene reductive dehalogenation*	-426.9	-1784	35.5:1	0.03:1

Table B.3.7 *Continued.*

Coupled Naphthalene Oxidation Reactions	$\Delta G°_r$ (kcal/ mole)	$\Delta G°_r$ (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$12O_2 + C_{10}H_8 \Rightarrow 10CO_2 + 4H_2O$ *Naphthalene oxidation /aerobic respiration*	-1217.40	-5094	3.00:1	0.33:1
$9.6NO_3^- + 9.6H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 8.8H_2O + 4.8N_2$ *Naphthalene oxidation / denitrification*	-1234.04	-5163	4.65:1	0.22:1
$24MnO_2 + 48H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 24Mn^{2+} + 28H_2O$ *Naphthalene oxidation / manganese reduction*	-1217.57	-5094	16.31:1	0.06:1
$48Fe(OH)_{3,a} + 96H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 48Fe^{2+} + 124H_2O$ *Naphthalene oxidation / iron reduction*	-932.64	-3902	40.13:1	0.02:1
$6SO_4^{2-} + 12H^+ + C_{10}H_8 \Rightarrow 10CO_2 + 6H_2S^o + 4H_2O$ ***Error! Switch argument not specified.****Naphthalene oxidation / sulfate reduction*	-196.98	-824.2	4.50:1	0.22:1
$8H_2O + C_{10}H_8 \Rightarrow 4CO_2 + 6CH_4$ *Naphthalene oxidation / methanogenesis*	-44.49	-186.1	1.13:1	0.88:1
$24C_2H_2Cl_4 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_3Cl_3 + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/ PCA reductive dehalogenation*	-511.68	-2139	31.1:1	0.03:1
$24C_2H_3Cl_3 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_4Cl_2 + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/ TCA reductive dehalogenation*	-589.09	-2462	24.8:1	0.04:1
$24C_2H_4Cl_2 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_5Cl + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/ DCA reductive dehalogenation*	-532.69	-2227	18.4:1	0.05:1
$24C_2Cl_4 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2HCl_3 + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/ Tetrachloroethylene reductive dehalogenation*	-566.59	-2371	31.1:1	0.03:1
$24C_2HCl_3 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_2Cl_2 + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/ Trichloroethylene reductive dehalogenation*	-552.91	-2313	24.6:1	0.04:1
$24C_2H_2Cl_2 + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_3Cl + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/cis-Dichloroethylene reductive dehalogenation*	-438.67	-1835	18.2:1	0.05:1
$24C_2H_3Cl + 20H_2O + C_{10}H_8 \Rightarrow 24C_2H_4 + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/ Vinyl chloride reductive dehalogenation*	-441.01	-1843	11.6:1	0.09:1
$24C_6Cl_6 + 20H_2O + C_{10}H_8 \Rightarrow 24C_6H_1Cl_5 + 10CO_2 + 24H^+ + 24Cl$ *Naphthalene oxidation/ Hexachlorobenzene reductive dehalogenation*	-545.94	-2282	52.9:1	0.02:1
$24C_6H_1Cl_5 + 20H_2O + C_{10}H_8 \Rightarrow 24C_6H_2Cl_4 + 10CO_2 + 24H^+ + 24Cl$ *Naphthalene oxidation/Pentachlorobenzene reductive dehalogenation*	-559.33	-2338	46.5:1	0.02:1
$24C_6H_2Cl_4 + 20H_2O + C_{10}H_8 \Rightarrow 24C_6H_3Cl_3 + 10CO_2 + 24H^+ + 24Cl$ *Naphthalene oxidation/ Tetrachlorobenzene reductive dehalogenation*	-512.53	-2142	40.1:1	0.02:1
$24C_6H_3Cl_3 + 20H_2O + C_{10}H_8 \Rightarrow 24C_6H_4Cl_2 + 10CO_2 + 24H^+ + 24Cl^-$ *Naphthalene oxidation/ Trichlorobenzene reductive dehalogenation*	-490.45	-2050	33.8:1	0.03:1

Table B.3.7 *Continued.*

Coupled 1,3,5-Trimethylbenzene (1,3,5-TMB) Oxidation Reactions	$\Delta G°_r$ (kcal/ mole)	$\Delta G°_r$ (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$12O_2 + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O$ *1,3,5-TMB oxidation /aerobic respiration*	-1213.29	-5076	3.20:1	0.31:1
$9.6NO_3^- + 9.6H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 10.8H_2O + 4.8N_{2,g}$ *1,3,5-TMB oxidation / denitrification*	-1229.93	-5146	4.96:1	0.20:1
$24MnO_2 + 48H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 30H_2O + 24Mn^{2+}$ *1,3,5-TMB oxidation / manganese reduction*	-1213.46	-5077	17.40:1	0.06:1
$48Fe(OH)_{3,a} + 96H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48Fe^{2+} + 126H_2O$ *1,3,5-TMB oxidation / iron reduction*	-928.53	-3885	42.80:1	0.02:1
$6SO_4^{2-} + 12H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O + 6H_2S^o$ *1,3,5-TMB oxidation / sulfate reduction*	-192.87	-807.0	4.80:1	0.21:1
$6H_2O + C_6H_3(CH_3)_3 \Rightarrow 3CO_2 + 6CH_4$ *1,3,5-TMB oxidation / methanogenesis*	-40.39	-169.0	0.90:1	1.11:1
$24\ C_2H_2Cl_4 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_3Cl_3 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-TMB oxidation/ PCA reductive dehalogenation*	-507.36	-2121	33.2:1	0.03:1
$24C_2H_3Cl_3 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_4Cl_2 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-TMB oxidation/ TCA reductive dehalogenation*	-584.99	-2445	26.4:1	0.04:1
$24C_2H_4Cl_2 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_5Cl + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-TMB oxidation/ DCA reductive dehalogenation*	-528.59	-2210	19.6:1	0.05:1
$24C_2Cl_4 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2HCl_3 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-TMB oxidation/ Tetrachloroethene reductive dehalogenation*	-562.48	-2353	33.2:1	0.03:1
$24C_2HCl_3 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_2Cl_2 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-TMB oxidation/ Trichloroethene reductive dehalogenation*	-548.80	-2296	26.3:1	0.04:1
$24C_2H_2Cl_2 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_3Cl + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-TMB oxidation/ cis-Dichloroethene reductive dehalogenation*	-434.56	-1818	19.4:1	0.05:1
$24C_2H_3Cl + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_4 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-TMB oxidation/ Vinyl chloride reductive dehalogenation*	-436.91	-1826	12.4:1	0.08:1
$24C_6Cl_6 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_6H_1Cl_5 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-TMB oxidation/ Hexachlorobenzene reductive dehalogenation*	-541.84	-2265	56.4:1	0.02:1
$24C_6H_1Cl_5 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_6H_2Cl_4 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-TMB oxidation/ Pentachlorobenzene reductive dehalogenation*	-555.23	-2321	49.6:1	0.02:1
$24C_6H_2Cl_4 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_6H_3Cl_3 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-TMB oxidation/ Tetrachlorobenzene reductive dehalogenation*	-508.43	-2125	42.8:1	0.02:1
$24C_6H_3Cl_3 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_6H_4Cl_2 + 9CO_2 + 24H^+ + 24Cl^-$ *1,3,5-TMB oxidation/ Trichlorobenzene reductive dehalogenation*	-486.35	-2033	36.0:1	0.03:1

Table B.3.7 *Continued.*

Coupled 1,2,4-Trimethylbenzene (1,2,4-TMB) Oxidation Reactions	$\Delta G°_r$ (kcal/ mole)	$\Delta G°_r$ (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$12O_2 + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O$ *1,2,4-TMB oxidation /aerobic respiration*	-1212.92	-5075	3.20:1	0.31:1
$9.6NO_3^- + 9.6H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 10.8H_2O + 4.8N_{2,g}$ *1,2,4-TMB oxidation / denitrification*	-1229.56	-5144	4.96:1	0.20:1
$24\underline{MnO_2} + 48H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 30H_2O + 24Mn^{2+}$ *1,2,4-TMB oxidation / manganese reduction*	-1213.09	-5076	17.4:1	0.06:1
$48\underline{Fe(OH)}_{3,a} + 96H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 48Fe^{2+} + 126H_2O$ *1,2,4-TMB oxidation / iron reduction*	-928.16	-3883	42.8:1	0.02:1
$6SO_4^{2-} + 12H^+ + C_6H_3(CH_3)_3 \Rightarrow 9CO_2 + 6H_2O + 6H_2S^o$ *1,2,4-TMB oxidation / sulfate reduction*	-192.50	-805.4	4.80:1	0.21:1
$6H_2O + C_6H_3(CH_3)_3 \Rightarrow 3CO_2 + 6CH_4$ *1,2,4-TMB oxidation / methanogenesis*	-40.02	-167.4	0.90:1	1.11:1
$24C_2H_2Cl_4 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_3Cl_3 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-TMB oxidation/ PCA reductive dehalogenation*	-507.36	-2121	33.2:1	0.03:1
$24C_2H_3Cl_3 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_4Cl_2 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-TMB oxidation/ TCA reductive dehalogenation*	-584.62	-2444	26.4:1	0.04:1
$24C_2H_4Cl_2 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_5Cl + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-TMB oxidation/ DCA reductive dehalogenation*	-528.22	-2208	19.6:1	0.05:1
$24C_2Cl_4 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2HCl_3 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-TMB oxidation/ PCE reductive dehalogenation*	-562.11	-2352	33.2:1	0.03:1
$24C_2HCl_3 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_2Cl_2 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-TMB oxidation/ TCE reductive dehalogenation*	-548.43	-2295	26.3:1	0.04:1
$24C_2H_2Cl_2 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_3Cl + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-TMB oxidation/ cis-DCE reductive dehalogenation*	-434.19	-1817	19.4:1	0.05:1
$24C_2H_3Cl + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_2H_4 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-TMB oxidation/ Vinyl chloride reductive dehalogenation*	-436.54	-1825	12.4:1	0.08:1
$24C_6Cl_6 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_6H_1Cl_5 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-TMB oxidation/ Hexachlorobenzene reductive dehalogenation*	-541.47	-2263	56.4:1	0.02:1
$24C_6H_1Cl_5 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_6H_2Cl_4 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-TMB oxidation/ Pentachlorobenzene reductive dehalogenation*	-554.86	-2319	49.6:1	0.02:1
$24C_6H_2Cl_4 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_6H_3Cl_3 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-TMB oxidation/ Tetrachlorobenzene reductive dehalogenation*	-508.06	-2124	42.8:1	0.02:1
$24C_6H_3Cl_3 + 18H_2O + C_6H_3(CH_3)_3 \Rightarrow 24C_6H_4Cl_2 + 9CO_2 + 24H^+ + 24Cl^-$ *1,2,4-TMB oxidation/ Trichlorobenzene reductive dehalogenation*	-485.98	-2031	36.0:1	0.03:1

Table B.3.7 *Continued.*

Coupled Vinyl Chloride Oxidation Reactions	$\Delta G°_r$ (kcal/ mole)	$\Delta G°_r$ (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$2.5O_2 + C_2H_3Cl \Rightarrow 2CO_2 + H_2O + H^+ + Cl^-$ *Vinyl Chloride oxidation /aerobic respiration*	-288.98	-1209	1.29:1	0.78:1
$2NO_3^- + H^+ C_2H_3Cl \Rightarrow 2CO_2 + 2H_2O + Cl^- + N_{2,g}$ *Vinyl Chloride oxidation / denitrification*	-292.44	-1224	2.00:1	0.50:1
$5\underline{MnO_2} + 9H^+ + C_2H_3Cl \Rightarrow 2CO_2 + 6H_2O + 5Mn^{2+} + Cl^-$ *Vinyl Chloride oxidation / manganese reduction*	-289.01	-1209	7.02:1	0.14:1
$10\underline{Fe(OH)_{3,a}} + 19H^+ + C_6H_3(CH_3)_3 \Rightarrow 2CO_2 + 10Fe^{2+} + 26H_2O + Cl^-$ *Vinyl Chloride oxidation / iron reduction*	-229.65	-960.9	17.3:1	0.06:1
$1.25SO_4^{2-} + 1.5H^+ + C_2H_3Cl \Rightarrow 2CO_2 + H_2O + 1.25H_2S^o + Cl^-$ *Vinyl Chloride oxidation / sulfate reduction*	-76.40	-319.7	1.94:1	0.52:1
$1.5H_2O + C_2H_3Cl \Rightarrow .75CO_2 + 1.25CH_4 + H^+ + Cl^-$ *Vinyl Chloride oxidation / methanogenesis*	-44.62	-186.7	0.44:1	2.27:1
$5C_2H_2Cl_4 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2H_3Cl_3 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ PCA reductive dehalogenation*	-141.90	-593.1	13.4:1	0.07:1
$5C_2H_3Cl_3 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2H_4Cl_2 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ TCA reductive dehalogenation*	-158.08	-661	10.7:1	0.09:1
$5C_2H_4Cl_2 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2H_5Cl + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ DCA reductive dehalogenation*	-146.33	-612	7.92:1	0.13:1
$5C_2Cl_4 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2HCl_3 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ DCE reductive dehalogenation*	-153.39	-641.8	13.4:1	0.07:1
$5C_2HCl_3 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2H_2Cl_2 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ TCE reductive dehalogenation*	-150.54	-629.9	10.6:1	0.09:1
$5C_2H_2Cl_2 + 4H_2O + C_2H_3Cl \Rightarrow 5C_2H_3Cl + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ cis-DCE reductive dehalogenation*	-126.74	-530.3	7.82:1	0.13:1
$5C_6Cl_6 + 4H_2O + C_2H_3Cl \Rightarrow 5C_6H_1Cl_5 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ Hexachlorobenzene reductive dehalogenation*	-144.60	-604.4	22.8:1	0.04:1
$5C_6H_1Cl_5 + 4H_2O + C_2H_3Cl \Rightarrow 5C_6H_2Cl_4 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ Pentachlorobenzene reductive dehalogenation*	-138.59	-579.3	20.0:1	0.05:1
$5C_6H_2Cl_4 + 4H_2O + C_2H_3Cl \Rightarrow 5C_6H_3Cl_3 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ Tetrachlorobenzene reductive dehalogenation*	-142.13	-594.1	17.3:1	0.06:1
$5C_6H_3Cl_3 + 4H_2O + C_2H_3Cl \Rightarrow 5C_6H_4Cl_2 + 2CO_2 + 6H^+ + 6Cl^-$ *Vinyl Chloride oxidation/ Trichlorobenzene reductive dehalogenation*	-137.53	-574.9	14.5:1	0.07:1
$2O_2 + C_2H_2Cl_2 \Rightarrow 2CO_2 + 2H^+ + 2Cl^-$ *DCE oxidation /aerobic respiration*	-256.53	-1072	1.31:1	0.76:1

Table B.3.7 *Continued.*

Coupled Chlorobenzene Oxidation Reactions	$\Delta G°_r$ (kcal/ mole)	$\Delta G°_r$ (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$7O_2 + C_6H_4Cl \Rightarrow 6CO_2 + H^+ + 2H_2O + Cl^-$ *Chlorobenzene oxidation /aerobic respiration*	-731.62	-3061	2.00:1	0.50:1
$5.6NO_3^- + 4.6H^+ + C_6H_4Cl \Rightarrow 6CO_2 + 4.8H_2O + 2.8N_{2,g} + 2Cl^-$ *Chlorobenzene oxidation / denitrification*	-741.33	-3102	3.10:1	0.32:1
$14\underline{MnO_2} + 27H^+ + C_6H_5Cl \Rightarrow 6CO_2 + 16H_2O + 14Mn^{2+} + Cl^-$ *Chlorobenzene oxidation / manganese reduction*	-731.72	-3062	10.9:1	0.09:1
$28\underline{Fe(OH)_{3,a}} + 55H^+ + C_6H_5Cl \Rightarrow 6CO_2 + 72H_2O + 28Fe^{2+} + Cl^-$ *Chlorobenzene oxidation / iron reduction*	-565.51	-2366	26.8:1	0.04:1
$3.5SO_4^{2-} + 6H^+ + C_6H_5Cl \Rightarrow 6CO_2 + 2H_2O + 3.5H_2S^o + Cl^-$ *Chlorobenzene oxidation / sulfate reduction*	-136.38	-570.6	3.00:1	0.33:1
$5H_2O + C_6H_5Cl \Rightarrow 2.5CO_2 + 3.5CH_4 + H^+ + Cl^-$ *Chlorobenzene oxidation / methanogenesis*	-47.43	-198.4	0.80:1	1.25:1
$14C_2H_2Cl_4 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_3Cl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ PCA reductive dehalogenation*	-320.04	-1338	20.8:1	0.05:1
$14C_2H_3Cl_3 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_4Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ TCA reductive dehalogenation*	-365.11	-1526	16.5:1	0.06:1
$14C_2H_4Cl_2 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_5Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ DCA reductive dehalogenation*	-332.21	-1389	12.3:1	0.08:1
$14C_2Cl_4 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2HCl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ PCE reductive dehalogenation*	-351.99	-1473	20.7:1	0.05:1
$14C_2HCl_3 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_2Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ TCE reductive dehalogenation*	-344.01	-1439	16.4:1	0.06:1
$14C_2H_2Cl_2 + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_3Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ cis-DCE reductive dehalogenation*	-277.37	-1161	12.1:1	0.08:1
$14C_2H_3Cl + 12H_2O + C_6H_5Cl \Rightarrow 14C_2H_4 + 6CO_2 + 15H^+ + 15Cl^-$ *Chlorobenzene oxidation/ Vinyl chloride reductive dehalogenation*	-278.73	-1165	7.75:1	0.13:1

Table B.3.7 *Continued.*

Coupled Dichlorobenzene Oxidation Reactions	$\Delta G°_r$ (kcal/ mole)	$\Delta G°_r$ (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$6.5O_2 + C_6H_4Cl_2 \Rightarrow 6CO_2 + 2H^+ + H_2O + 2Cl^-$ *Dichlorobenzene oxidation /aerobic respiration*	-698.36	-2919	1.42:1	0.70:1
$5.2NO_3^- + 3.2H^+ + C_6H_4Cl_2 \Rightarrow 6CO_2 + 3.6H_2O + 2.6N_{2,g} + 2Cl^-$ *Dichlorobenzene oxidation / denitrification*	-708.76	-2963	1.64:1	0.61:1
$13\underline{MnO_2} + 24H^+ + C_6H_4Cl_2 \Rightarrow 6CO_2 + 14H_2O + 13Mn^{2+} + 2Cl^-$ *Dichlorobenzene oxidation / manganese reduction*	-698.36	-2919	7.75:1	0.13:1
$26\underline{Fe(OH)}_{3,a} + 50H^+ + C_6H_4Cl_2 \Rightarrow 6CO_2 + 66H_2O + 26Fe^{2+} + 2Cl^-$ *Dichlorobenzene oxidation / iron reduction*	-521.56	-2180	19.05:1	0.05:1
$3.25SO_4^{2-} + 4.5H^+ + C_6H_4Cl_2 \Rightarrow 6CO_2 + H_2O + 3.25H_2S^o + 2Cl^-$ *Dichlorobenzene oxidation / sulfate reduction*	-142.74	-596.7	2.14:1	0.47:1
$5.5H_2O + C_6H_4Cl_2 \Rightarrow 2.75CO_2 + 3.25CH_4 + 2H^+ + 2Cl^-$ *Dichlorobenzene oxidation / methanogenesis*	-64.22	-268.4	0.33:1	2.99:1
$13C_2H_2Cl_4 + 12H_2O + C_6H_4Cl_2 \Rightarrow 13C_2H_3Cl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Dichlorobenzene oxidation/ PCA reductive dehalogenation*	-317.20	-1326	14.8:1	0.07:1
$13C_2H_3Cl_3 + 12H_2O + C_6H_4Cl_2 \Rightarrow 13C_2H_4Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Dichlorobenzene oxidation/ TCA reductive dehalogenation*	-358.93	-1500	11.8:1	0.09:1
$13C_2H_4Cl_2 + 12H_2O + C_6H_4Cl_2 \Rightarrow 13C_2H_5Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Dichlorobenzene oxidation/ DCA reductive dehalogenation*	-328.38	-1373	8.73:1	0.11:1
$13C_2Cl_4 + 12H_2O + C_6H_4Cl_2 \Rightarrow 13C_2HCl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Dichlorobenzene oxidation/ PCE reductive dehalogenation*	-347.10	-1450	14.6:1	0.07:1
$13C_2HCl_3 + 12H_2O + C_6H_4Cl_2 \Rightarrow 13C_2H_2Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Dichlorobenzene oxidation/ TCE reductive dehalogenation*	-339.56	-1419	11.6:1	0.09:1
$13C_2H_2Cl_2 + 12H_2O + C_6H_4Cl_2 \Rightarrow 13C_2H_3Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Dichlorobenzene oxidation/ cis-DCE reductive dehalogenation*	-277.68	-1161	8.55:1	0.12:1
$13C_2H_3Cl + 12H_2O + C_6H_4Cl_2 \Rightarrow 13C_2H_4 + 6CO_2 + 15H^+ + 15Cl^-$ *Dichlorobenzene oxidation/ Vinyl chloride reductive dehalogenation*	-278.72	-1165	5.52:1	0.18:1

Table B.3.7 *Continued.*

Coupled Trichlorobenzene Oxidation Reactions	$\Delta G°_r$ (kcal/ mole)	$\Delta G°_r$ (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$6O_2 + C_6H_3Cl_3 \Rightarrow 6CO_2 + 3H^+ + 3Cl^-$ *Trichlorobenzene oxidation /aerobic respiration*	-668.16	-2793	1.07:1	0.94:1
$4.8NO_3^- + 1.8H^+ + C_6H_3Cl_3 \Rightarrow 6CO_2 + 2.4H_2O + 2.4N_{2,g} + 3Cl^-$ *Trichlorobenzene oxidation / denitrification*	-677.76	-2833	1.65:1	0.60:1
$12\underline{MnO_2} + 21H^+ + C_6H_3Cl_3 \Rightarrow 6CO_2 + 12H_2O + 12Mn^{2+} + 3Cl^-$ *Trichlorobenzene oxidation / manganese reduction*	-688.16	-2793	5.80:1	0.17:1
$24\underline{Fe(OH)}_{3,a} + 45H^+ + C_6H_3Cl_3 \Rightarrow 6CO_2 + 60H_2O + 24Fe^{2+} + 3Cl^-$ *Trichlorobenzene oxidation / iron reduction*	-504.96	-2111	14.3:1	0.07:1
$3SO_4^{2-} + 3H^+ + C_6H_3Cl_3 \Rightarrow 6CO_2 + 3H_2S^o + 3Cl^-$ *Trichlorobenzene oxidation / sulfate reduction*	-155.28	-649.1	1.60:1	0.63:1
$6H_2O + C_6H_3Cl_3 \Rightarrow 3CO_2 + 3CH_4 + 3H^+ + 3Cl^-$ *Trichlorobenzene oxidation / methanogenesis*	-82.80	-346.1	0.25:1	4.00:1
$12C_2H_2Cl_4 + 12H_2O + C_6H_3Cl_3 \Rightarrow 12C_2H_3Cl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Trichlorobenzene oxidation/ PCA reductive dehalogenation*	-316.32	-1322	11.1:1	0.09:1
$12C_2H_3Cl_3 + 12H_2O + C_6H_3Cl_3 \Rightarrow 12C_2H_4Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Trichlorobenzene oxidation/ TCA reductive dehalogenation*	-354.82	-1483	8.8:1	0.11:1
$12C_2H_4Cl_2 + 12H_2O + C_6H_3Cl_3 \Rightarrow 12C_2H_5Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Trichlorobenzene oxidation/ DCA reductive dehalogenation*	-326.62	-1365	6.53:1	0.15:1
$12C_2Cl_4 + 12H_2O + C_6H_3Cl_3 \Rightarrow 12C_2HCl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Trichlorobenzene oxidation/ PCE reductive dehalogenation*	-343.92	-1438	10.9:1	0.09:1
$12C_2HCl_3 + 12H_2O + C_6H_3Cl_3 \Rightarrow 12C_2H_2Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Trichlorobenzene oxidation/ TCE reductive dehalogenation*	-336.96	-1408	8.67:1	0.12:1
$12C_2H_2Cl_2 + 12H_2O + C_6H_3Cl_3 \Rightarrow 12C_2H_3Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Trichlorobenzene oxidation/ cis-DCE reductive dehalogenation*	-279.58	-1169	6.40:1	0.16:1
$12C_2H_3Cl + 12H_2O + C_6H_3Cl_3 \Rightarrow 12C_2H_4 + 6CO_2 + 15H^+ + 15Cl^-$ *Trichlorobenzene oxidation/ Vinyl chloride reductive dehalogenation*	-280.78	-1174	4.13:1	0.24:1

Table B.3.7 *Continued.*

Coupled Tetrachlorobenzene Oxidation Reactions	$\Delta G°_r$ (kcal/ mole)	$\Delta G°_r$ (kJ/ mole)	Stoichiometric Mass Ratio of Electron Acceptor or Metabolic Byproduct to Primary Substrate	Mass of Primary Substrate Utilized per Mass of Electron Acceptor Utilized or Metabolic Byproduct Produced
$5.5O_2 + H_2O + C_6H_2Cl_4 \Rightarrow 6CO_2 + 4H^+ + 4Cl^-$ *Tetrachlorobenzene oxidation /aerobic respiration*	-639.10	-2671	0.82:1	1.22:1
$4.4NO_3^- + 0.4\ H^+ + C_6H_2Cl_4 \Rightarrow 6CO_2 + 1.2H_2O + 2.2N_{2,g} + 4Cl^-$ *Tetrachlorobenzen oxidation / denitrification*	-647.90	-2708	1.27:	0.78:1
$11\underline{MnO_2} + 18H^+ + C_6H_2Cl_4 \Rightarrow 6CO_2 + 10H_2O + 11Mn^{2+} + 4Cl^-$ *Tetrachlorobenzenoxidation / manganese reduction*	-639.10	-2671	4.47:1	0.22:1
$22\underline{Fe(OH)}_{3,a} + 40H^+ + C_6H_2Cl_4 \Rightarrow 6CO_2 + 54H_2O + 22Fe^{2+} + 4Cl^-$ *Tetrachlorobenzen oxidation / iron reduction*	-489.50	-2046	11.0:1	0.09:1
$2.75SO_4^{2-} + 1.75H^+ + H_2O + C_6H_2Cl_4 \Rightarrow 6CO_2 + 2.75H_2S^o + 4Cl^-$ *Tetrachlorobenzen oxidation / sulfate reduction*	-168.96	-706.3	1.23:1	0.81:1
$6.5H_2O + C_6H_2Cl_4 \Rightarrow 3.25CO_2 + 2.75CH_4 + 4H^+ + 4Cl^-$ *Tetrachlorobenzen oxidation / methanogenesis*	-102.52	-428.5	0.19:1	5.19:1
$11C_2H_2Cl_4 + 12H_2O + C_6H_2Cl_4 \Rightarrow 11C_2H_3Cl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Tetrachlorobenzen oxidation/ PCA reductive dehalogenation*	-287.01	-1200	8.53:1	0.12:1
$11C_2H_3Cl_3 + 12H_2O + C_6H_2Cl_4 \Rightarrow 11C_2H_4Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Tetrachlorobenzen oxidation/ TCA reductive dehalogenation*	-323.64	-1353	6.79:1	0.15:1
$11C_2H_4Cl_2 + 12H_2O + C_6H_2Cl_4 \Rightarrow 11C_2H_5Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Tetrachlorobenzen oxidation/ DCA reductive dehalogenation*	-297.79	-1392	5.04:1	0.20:1
$11C_2Cl_4 + 12H_2O + C_6H_2Cl_4 \Rightarrow 11C_2HCl_3 + 6CO_2 + 15H^+ + 15Cl^-$ *Tetrachlorobenzen oxidation/ PCE reductive dehalogenation*	-313.3	-1310	8.43:1	0.12:1
$11C_2HCl_3 + 12H_2O + C_6H_2Cl_4 \Rightarrow 11C_2H_2Cl_2 + 6CO_2 + 15H^+ + 15Cl^-$ *Tetrachlorobenzen oxidation/ TCE reductive dehalogenation*	-307.03	-1283	6.68:1	0.15:1
$11C_2H_2Cl_2 + 12H_2O + C_6H_2Cl_4 \Rightarrow 11C_2H_3Cl + 6CO_2 + 15H^+ + 15Cl^-$ *Tetrachlorobenzen oxidation/ cis-DCE reductive dehalogenation*	-254.67	-1065	4.93:1	0.20:1
$11C_2H_3Cl + 12H_2O + C_6H_2Cl_4 \Rightarrow 11C_2H_4 + 6CO_2 + 15H^+ + 15Cl^-$ *Tetrachlorobenzen oxidation/ Vinyl chloride reductive dehalogenation*	-255.77	-1069	3.19:1	0.31:1

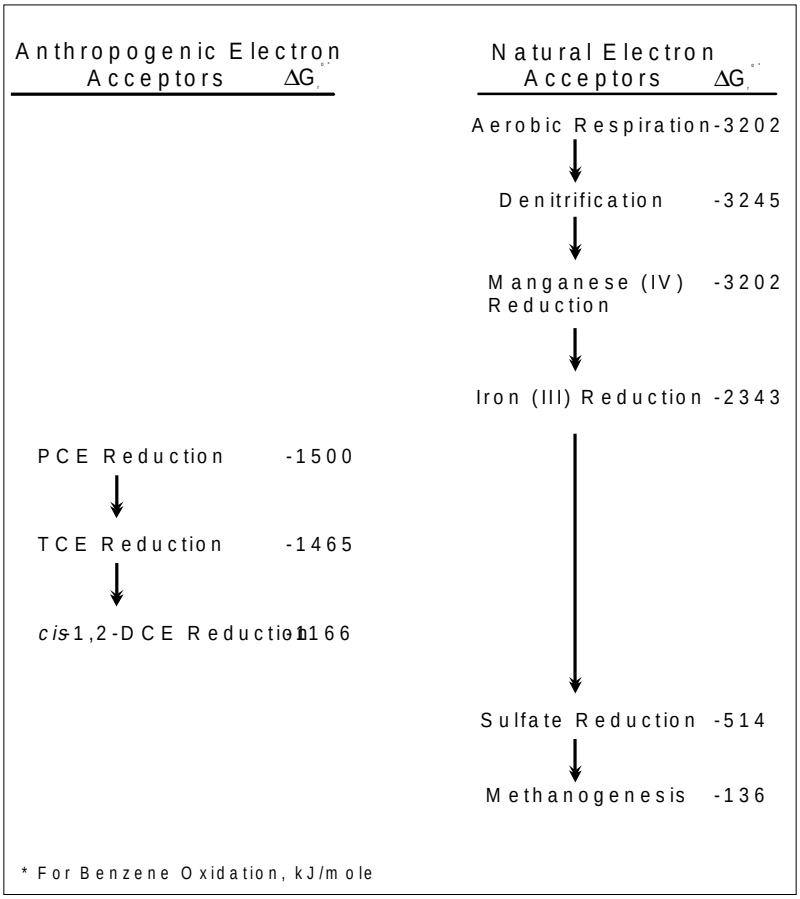

Figure B.3.4 *Expected sequence of microbially-mediated redox reactions and Gibbs free energy of reaction.*

B.3.6 ONE-DIMENSIONAL ADVECTION-DISPERSION EQUATION WITH RETARDATION AND BIODEGRADATION

The advection-dispersion equation is obtained by adding a biodegradation term to equation B.2.20. In one dimension, this is expressed as:

$$\frac{\partial C}{\partial t} = \frac{D_x}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R}\frac{\partial C}{\partial x} - \lambda C \qquad \text{eq. B.3.2}$$

Where:

v_x = average linear ground-water velocity [L/T]
R = coefficient of retardation
C = contaminant concentration [M/L^3]
D_x = hydrodynamic dispersion [L^2/T]
t = time [T]
x = distance along flow path [L]
λ = first-order biodegradation decay rate [T^{-1}]

This equation considers advection, hydrodynamic dispersion, sorption (retardation), and biodegradation. First-order rate constants are appropriate for iron (III)-reducing, sulfate-reducing, and methanogenic conditions. They are not appropriate under aerobic or denitrifying conditions.

SECTION B-4
DESTRUCTIVE ATTENUATION MECHANISMS - ABIOTIC

Chlorinated solvents dissolved in ground water may also be degraded by abiotic mechanisms, although the reactions are typically not complete and often result in the formation of an intermediate that may be at least as toxic as the original contaminant. The most common reactions affecting chlorinated compounds are hydrolysis (a substitution reaction) and dehydrohalogenation (an elimination reaction). Other possible reactions include oxidation and reduction reactions. Butler and Barker (1996) note that no abiotic oxidation reactions involving typical halogenated solvents have been reported in the literature. They also note that reduction reactions (which include hydrogenolysis and dihaloelimination) are commonly microbially mediated, although some abiotic reduction reactions have been observed.

As Butler and Barker (1996) note, attributing changes in either the presence or absence of halogenated solvents or the concentrations of halogenated solvents to abiotic processes is usually difficult. For example, microbial activity is generally required to produce reducing conditions that favor reductive dehalogenation. If such activity is taking place, chlorinated solvents may be undergoing both biotic and abiotic degradation, and discerning the relative contribution of each mechanism on the field scale, if possible, would be very difficult. As another example, Butler and Barker (1996) note that to substantiate that hydrolysis is occurring, the presence of non-halogenated breakdown products such as acids and alcohols should be established. In general, these products are more easily biodegraded than their parent compounds and can be difficult to detect. Field evidence of this nature has yet to be collected to demonstrate hydrolysis of halogenated solvents (Butler and Barker, 1996).

Given the difficulties of demonstrating abiotic degradation on the field scale, it may not be practical to demonstrate that such processes are occurring and to quantitatively evaluate the contributions of those reactions (i.e., separately from biotic processes). If biodegradation is occurring at a site, the loss of contaminant mass due to that process may dwarf the mass lost to abiotic reactions, ruling out a cost-effective evaluation of abiotic degradation. However, while the rates of abiotic degradation may be slow relative to biotic mechanisms, the contribution of these mechanisms may still play a significant role in natural attenuation, depending on site conditions (e.g., a site with a slow solute transport velocity or a long distance to the nearest receptor). Vogel (1994) describes data patterns that may result from varying combinations of biotic and abiotic degradation of chlorinated solvents. Moreover, because some of the by-products of these reactions are chlorinated compounds that may be more easily or less easily degraded than the parent, the contributions of abiotic mechanisms may need to be considered when evaluating analytical data from a site.

B.4.1 HYDROLYSIS AND DEHYDROHALOGENATION

As discussed by Butler and Barker (1996), hydrolysis and dehydrohalogenation reactions are the most thoroughly studied abiotic attenuation mechanisms. In general, the rates of these reactions are often quite slow within the range of normal ground-water temperatures, with half-lives of days to centuries (Vogel *et al.*, 1987; Vogel, 1994). Therefore, most information about the rates of these reactions is extrapolated from experiments run at higher temperatures so that the experiments could be performed within a practical time frame.

B.4.1.1 Hydrolysis

Hydrolysis is a substitution reaction in which an organic molecule reacts with water or a component ion of water, and a halogen substituent is replaced with a hydroxyl (OH^-) group. The hydroxyl substitution typically occurs at the halogenated carbon. This leads initially to the production of alcohols. If the alcohols are halogenated, additional hydrolysis to acids or diols may occur. Also,

the addition of a hydroxyl group to a parent molecule may make the daughter product more susceptible to biodegradation, as well as more soluble (Neely, 1985). Non-alcohol products have also been reported by Vogel *et al*. (1987) and Jeffers *et al*. (1989), but they are apparently products of competing dehydrohalogenation reactions.

The likelihood that a halogenated solvent will undergo hydrolysis depends in part on the number of halogen substituents. More halogen substituents on a compound will decrease the chance for hydrolysis reactions to occur (Vogel *et al*., 1987), and will therefore decrease the rate of the reaction. In addition, bromine substituents are more susceptible to hydrolysis than chlorine substituents (Vogel *et al*., 1987). 1,2-Dibromoethane is one compound that is subject to significant hydrolysis reactions under natural conditions. Locations of the halogen substituent on the carbon chain may also have some effect on the rate of reaction. The rate also may increase with increasing pH; however, a rate dependence upon pH is typically not observed below a pH of 11 (Mabey and Mill, 1978; Vogel and Reinhard, 1986). Rates of hydrolysis may also be increased by the presence of clays, which can act as catalysts (Vogel *et al*., 1987). Hydrolysis rates can generally be described using first-order kinetics, particularly in solutions in which water is the dominant nucleophile (Vogel *et al*., 1987). However, this oversimplifies what is typically a much more complicated relationship (Neely, 1985). As noted in the introduction to this Appendix, reported rates of environmentally significant hydrolysis reactions involving chlorinated solvents are typically the result of extrapolation from experiments performed at higher temperatures (Mabey and Mill, 1978; Vogel, 1994).

Hydrolysis of chlorinated methanes and ethanes has been well-demonstrated in the literature. Vogel (1994) reports that monohalogenated alkanes have half-lives on the order of days to months, while polychlorinated methanes and ethanes have half-lives that may range up to thousands of years for carbon tetrachloride. As the number of chlorine atoms increases, dehydrohalogenation may become more important (Jeffers *et al*., 1989). Butler and Barker (1996) note that chlorinated ethenes do not undergo significant hydrolysis reactions (i.e., the rates are slow). Butler and Barker also reported that they were unable to find any studies on hydrolysis of vinyl chloride. A listing of half-lives for abiotic hydrolysis and dehydrohalogenation of some chlorinated solvents is presented on Table B.4.1. Note that no distinctions are made in the table as to which mechanism is operating; this is consistent with the references from which the table has been derived (Vogel *et al*., 1987; Butler and Barker, 1996).

One common chlorinated solvent for which abiotic transformations have been well-studied is 1,1,1-TCA. 1,1,1-TCA may be abiotically transformed to acetic acid through a series of substitution reactions, including hydrolysis. In addition, 1,1,1-TCA may be reductively dehalogenated to form 1,1- DCA) and then chloroethane (CA), which is then hydrolyzed to ethanol (Vogel and McCarty, 1987) or dehydrohalogenated to vinyl chloride (Jeffers *et al*., 1989). Rates of these reactions have been studied by several parties, and these rates are summarized in Table B.4.1.

B.4.1.2 Dehydrohalogenation

Dehydrohalogenation is an elimination reaction involving halogenated alkanes in which a halogen is removed from one carbon atom, followed by the subsequent removal of a hydrogen atom from an adjacent carbon atom. In this two-step reaction, an alkene is produced. Although the oxidation state of the compound decreases due to the removal of a halogen, the loss of a hydrogen atom increases it. This results in no external electron transfer, and there is no net change in the oxidation state of the reacting molecule (Vogel *et al*., 1987). Contrary to the patterns observed for hydrolysis, the likelihood that dehydrohalogenation will occur increases with the number of halogen substituents. It has been suggested that under normal environmental conditions, monohalogenated aliphatics apparently do not undergo dehydrohalogenation, and these reactions are apparently not likely to occur (March, 1985; Vogel *et al*., 1987). However, Jeffers *et al*. (1989) report on the

dehydrohalogenation of CA to VC. Polychlorinated alkanes have been observed to undergo dehydrohalogenation under normal conditions and extremely basic conditions (Vogel *et al*., 1987). As with hydrolysis, bromine substituents are more reactive with respect to dehydrohalogenation.

Table B.4.1 *Approximate Half-Lives of Abiotic Hydrolysis andDehydrohalogenation Reactions Involving Chlorinated Solvents*

Compound	Half-Life (years)	Products
Chloromethane	no data	
Methylene Chloride (Dichloromethane)	704[a/]	
Trichloromethane (Chloroform)	3500[a], 1800[b]	
Carbon Tetrachloride	41[b]	
Chloroethane	0.12[c]	ethanol
1,1-Dichloroethane	61[b]	
1,2-Dichloroethane	72[b]	
1,1,1-Trichloroethane	1.7[a], 1.1[b] 2.5[d]	acetic acid 1,1-DCE
1,1,2-Trichloroethane	140[b], 170[a]	1,1-DCE
1,1,1,2-Tetrachloroethane	47[b], 380[a]	TCE
1,1,2,2-Tetrachloroethane	0.3[e] 0.4[b], 0.8[a]	1,1,2-TCA TCE
Tetrachloroethene	0.7[f] *, 1.3 x 10[6 b]	
Trichloroethene	0.7[f] *, 1.3 x 10[6 b]	
1,1-Dichloroethene	1.2 x 10[8 b]	
1,2-Dichloroethene	2.1 x 10[10 b]	

[a] From Mabey and Mill, 1978
[b] From Jeffers *et al*., 1989
[c] From Vogel *et al*., 1987
[d] From Vogel and McCarty, 1987
[e] From Cooper *et al*., 1987
[f] From Dilling *et al*., 1975
* Butler and Barker (1996) indicate that these values may reflect experimental difficulties and that the longer half-life [as calculated by Jeffers et al. (1989)] should be used.

Dehydrohalogenation rates may also be approximated using pseudo-first-order kinetics. Once again, this is not truly a first-order reaction, but such approximations have been used in the literature to quantify the reaction rates. The rates will not only depend upon the number and types of halogen substituent, but also on the hydroxide ion concentration. Under normal pH conditions (i.e., near a

pH of 7), interaction with water (acting as a weak base) may become more important (Vogel *et al*., 1987). Transformation rates for dehydrohalogenation reactions is presented in Table B.4.1. 1,1,1-TCA is also known to undergo dehydrohalogenation (Vogel and McCarty, 1987). In this case, TCA is transformed to 1,1-DCE, which is then reductively dehalogenated to VC. The VC is then either reductively dehalogenated to ethene or consumed as a substrate in an aerobic reaction and converted to CO_2. In a laboratory study, Vogel and McCarty (1987) reported that the abiotic conversion of 1,1,1-TCA to 1,1-DCE has a rate constant of about 0.04 $year^{-1}$. It was noted that this result was longer than indicated in previous studies, but that experimental methods differed. Jeffers *et al*. (1989) reported on several other dehydrohalogenation reactions; in addition to 1,1,1-TCA and 1,1,2-TCA both degrading to 1,1-DCE, the tetrachloroethanes and pentachloroethanes degrade to TCE and PCE, respectively. Rates of these reactions are included in Table B.4.1. As noted previously, Jeffers *et al*. (1989) also report that CA may degrade to VC, but no information on rates was encountered during the literature search for this Appendix.

B.4.2 REDUCTION REACTIONS

Two abiotic reductive dechlorination reactions that may operate in the subsurface are hydrogenolysis and dihaloelimination. Hydrogenolysis is the simple replacement of a chlorine (or another halogen) by a hydrogen, while dihaloelimination is the removal of two chlorines (or other halogens) accompanied by the formation of a double carbon-carbon bond. Butler and Barker (1996) review work by Criddle *et al*. (1986), Jafvert and Wolfe (1987), Reinhard *et al*. (1990), and Acton (1990) and this review suggests that while these reactions are thermodynamically possible under reducing conditions, they often do not take place in the absence of biological activity, even if such activity is only indirectly responsible for the reaction. While not involved in a manner similar to that for cometabolism, microbes may produce reductants that facilitate such reactions in conjunction with minerals in the aquifer matrix, as has been suggested by work utilizing aquifer material from the Borden test site (Reinhard *et al*., 1990). Moreover, the reducing conditions necessary to produce such reactions are most often created as a result of microbial activity. It is therefore not clear if some of these reactions are truly abiotic, or if because of their reliance on microbial activity to produce reducing conditions or reactants, they should be considered to be a form of cometabolism.

In some cases, truly abiotic reductive dechlorination has been observed; however, the conditions that favor such reactions may not occur naturally. For example, Gillham and O'Hannesin (1994) describe reductive dehalogenation of chlorinated aliphatics using zero-valent iron, in which the iron serves as an electron donor in an electrochemical reaction. However, this is not a natural process. Wang and Tan (1990) reported reduction of TCE to ethene and carbon tetrachloride to methane during a platinum-catalyzed reaction between elemental magnesium and water. Given that the metals involved in these reactions are unlikely to occur naturally in the reduced forms used in the aforementioned work, such processes are not likely to contribute to natural attenuation of chlorinated solvents.